

Handbook on the Physics and Chemistry of Rare Earths, volume 22

Elsevier, 1996

Edited by: Karl A. Gschneidner, Jr. and LeRoy Eyring ISBN: 978-0-444-82288-8

PREFACE

Karl A. GSCHNEIDNER, Jr., and LeRoy EYRING

These elements perplex us in our rearches [sic], baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us – mocking, mystifying, and murmuring strange revelations and possibilities.

Sir William Crookes (February 16, 1887)

Various physical aspects of a wide range of rare-earth materials are covered in this volume. Magnetic phenomena dominate the contents of the first four chapters which deal with thin films and layered structures, and intermetallic and nonmetallic compounds. The remaining two chapters deal with coherent emission and electronic structure calculations of lanthanide molecules.

In the lead-off chapter (147) Flynn and Salamon cover the state-of-the-art of the synthesis and properties of thin films of the rare-earth metals and layered superstructures of two rare-earth metals. Although films of rare-earth metals have been studied for about 25 years, the availability of high-quality, well-characterized materials dates back about 10 years to the mid-1980's. Thus, we are only at the early stages of knowledge and understanding of the behaviors and properties of these two-dimensional materials. Flynn and Salamon describe the progress that has been made in the study of epitaxial rare earths in general and their superlattices in particular, and clarify the principles common to all rare-earth-rare-earth thin film magnetic systems.

The first chapter is followed by a companion review of rare-earth-transition-metal nanoscale multilayers. Work on these materials is driven, not only by our quest for basic knowledge, but by possible applications for perpendicular-magnetic and magneto-optical recording. In chapter 148 Shan and Sellmyer describe the recent advances in our understanding of magnetic structure, interfacial magnetism, and origin of perpendicular magnetic anisotropy of lanthanide-transition-metal nanoscale multilayers.

One of the important series of rare-earth intermetallic compounds are those which possess the $ThMn_{12}$ -type structure. Generally, these compounds form as ternary phases with only a handful of binary compounds known to exist. As pointed out in the review by Suski (chapter 149) there are two distinct subgroups in this family of compounds: those with a relatively low content of transition element (Fe, Co and Ni) and those with a high content of these metals. The first group of compounds are stabilized by Al, Ga and In,

PREFACE

while the second group of phases are stabilized by Si, Ti, V, Cr, Mn, Mo and Re. The main emphasis in Suski's chapter is the magnetic behaviors of these phases, but structural and phase relations are also covered.

The sesquicentennial chapter of this Handbook series deals with the magnetic behaviors of dielectric lanthanide compounds, in particular the ethylsulfates $[R(C_2H_5SO_4)_3\cdot 9H_2O]$, the RLiF₄ tetrafluoride compounds with the scheelite-type structure, the zircon-type RMO₄ phases, the binary trifluorides (RF₃) and the cubic elpasolites, which have the general formula A₂BRX₆ where A = Rb, Cs; B = Li, Na; and X = F, Cl, Br, I. In chapter 150 Aminov, Malkin and Teplov review the specific magnetic and magnetoelastic properties of these crystals, which are determined by the localized electronic magnetic moments of the lanthanide ions in the crystal lattice and their interactions with each other and surrounding ions.

Auzel's chapter on coherent emission is different from many reviews on the subject, which are concerned with the laser effect itself, in that he concentrates on the broader issues. The emphasis of chapter 151 is on superradiance, superfluorescence, amplification of spontaneous emission by other stimulated emission than the laser effect, and coherent spontaneous emission. Also discussed are up-conversion by energy transfer, up-conversion by the avalanche effect, and recent advances in lanthanide lasers and amplifiers.

The final chapter (152) is by Dolg and Stoll in which they describe the progress that has been made in electronic structure calculations of lanthanide-containing molecules, especially in the last 10 years. The major problem is that lanthanide systems are quite complex, and in order to obtain meaningful results one needs to include both relativistic and electronic correlation effects. But with the availability of powerful computational resources and improved atomic structure codes, significant advances have been made. In addition to the lanthanide atoms themselves, quantum-chemical calculations have been made on diatomic molecules (e.g. dimers, monoxides, and monohydrides), simple polyatomic molecules (such as the hydrides, halides, and oxides), complex polyatomic molecules (which include fullerene complexes, hydrated ions, and sandwich complexes) and clusters that serve as models for segments of solids (such as RF_8^{5-} embedded in a CaF₂ matrix, Eu³⁺ impurity in GdBa₂NbO₆, and Ce centers in BaF₂, LaF₃ and YAlO₃). Just a few years ago (1988) C.K. Jørgensen, in his review on Influence of Rare Earths on Chemical Understanding and Classification (Vol. 11, ch. 75 of this Handbook series), posed the question "Is quantum chemistry feasible?", and with regard to the rare-earth elements, he answered "Sorry, not today; perhaps next century". But as Dolg and Stoll point out, the next century is only a few years away. In view of the progress to date, the editors believe we may even make it with a few years to spare.

October 19, 1995

CONTENTS

Preface v

Contents vii

Contents of Volumes 1-21 ix

- 147. C.P. Flynn and M.B. Salamon Synthesis and properties of single-crystal nanostructures 1
- 148. Z.S. Shan and D.J. Sellmyer Nanoscale rare earth-transition metal multilayers: magnetic structure and properties 81
- 149. W. Suski The ThMn₁₂-type compounds of rare earths and actinides: structure, magnetic and related properties 143
- 150. L.K. Aminov, B.Z. Malkin and M.A. Teplov Magnetic properties of nonmetallic lanthanide compounds 295
- 151. F. Auzel Coherent emission in rare-earth materials 507
- 152. M. Dolg and H. Stoll Electronic structure calculations for molecules containing lanthanide atoms 607

Author Index 731

Subject Index 777

CONTENTS OF VOLUMES 1–21

VOLUME 1: Metals

1978, 1st repr. 1982, 2nd repr. 1991; ISBN 0-444-85020-1

- 1. Z.B. Goldschmidt, Atomic properties (free atom) 1
- 2. B.J. Beaudry and K.A. Gschneidner Jr, Preparation and basic properties of the rare earth metals 173
- 3. S.H. Liu, Electronic structure of rare earth metals 233
- 4. D.C. Koskenmaki and K.A. Gschneidner Jr, Cerium 337
- 5. L.J. Sundström, Low temperature heat capacity of the rare earth metals 379
- 6. K.A. McEwen, Magnetic and transport properties of the rare earths 411
- 7. S.K. Sinha, Magnetic structures and inelastic neutron scattering: metals, alloys and compounds 489
- 8. T.E. Scott, Elastic and mechanical properties 591
- 9. A. Jayaraman, High pressure studies: metals, alloys and compounds 707
- 10. C. Probst and J. Wittig, Superconductivity: metals, alloys and compounds 749
- 11. M.B. Maple, L.E. DeLong and B.C. Sales, Kondo effect: alloys and compounds 797
- 12. M.P. Dariel, *Diffusion in rare earth metals* 847 Subject index 877

VOLUME 2: Alloys and intermetallics

1979, 1st repr. 1982, 2nd repr. 1991; ISBN 0-444-85021-X

- 13. A. Iandelli and A. Palenzona, Crystal chemistry of intermetallic compounds 1
- 14. H.R. Kirchmayr and C.A. Poldy, Magnetic properties of intermetallic compounds of rare earth metals 55
- 15. A.E. Clark, Magnetostrictive RFe2 intermetallic compounds 231
- 16. J.J. Rhyne, Amorphous magnetic rare earth alloys 259
- 17. P. Fulde, Crystal fields 295
- 18. R.G. Barnes, NMR, EPR and Mössbauer effect: metals, alloys and compounds 387
- 19. P. Wachter, Europium chalcogenides: EuO, EuS, EuSe and EuTe 507
- A. Jayaraman, Valence changes in compounds 575 Subject index 613

VOLUME 3: Non-metallic compounds – I

1979, 1st repr. 1984; ISBN 0-444-85215-8

- 21. L.A. Haskin and T.P. Paster, Geochemistry and mineralogy of the rare earths 1
- 22. J.E. Powell, Separation chemistry 81
- 23. C.K. Jørgensen, Theoretical chemistry of rare earths 111
- 24. W.T. Carnall, The absorption and fluorescence spectra of rare earth ions in solution 171
- 25. L.C. Thompson, Complexes 209
- 26. G.G. Libowitz and A.J. Maeland, Hydrides 299
- 27. L. Eyring, The binary rare earth oxides 337
- 28. D.J.M. Bevan and E. Summerville, Mixed rare earth oxides 401
- 29. C.P. Khattak and F.F.Y. Wang, Perovskites and garnets 525
- L.H. Brixner, J.R. Barkley and W. Jeitschko, Rare earth molybdates (VI) 609 Subject index 655

VOLUME 4: Non-metallic compounds – II

1979, 1st repr. 1984; ISBN 0-444-85216-6

- 31. J. Flahaut, Sulfides, selenides and tellurides 1
- 32. J.M. Haschke, Halides 89
- 33. F. Hulliger, Rare earth pnictides 153
- 34. G. Blasse, Chemistry and physics of R-activated phosphors 237
- 35. M.J. Weber, Rare earth lasers 275
- 36. F.K. Fong, Nonradiative processes of rare-earth ions in crystals 317
- 37A. J.W. O'Laughlin, Chemical spectrophotometric and polarographic methods 341
- 37B. S.R. Taylor, Trace element analysis of rare earth elements by spark source mass spectroscopy 359
- 37C. R.J. Conzemius, Analysis of rare earth matrices by spark source mass spectrometry 377
- 37D. E.L. DeKalb and V.A. Fassel, Optical atomic emission and absorption methods 405
- 37E. A.P. D'Silva and V.A. Fassel, X-ray excited optical luminescence of the rare earths 441
- 37F. F.W.V. Boynton, Neutron activation analysis 457
- 37G. S. Schuhmann and J.A. Philpotts, Mass-spectrometric stable-isotope dilution analysis for lanthanides in geochemical materials 471
- 38. J. Reuben and G.A. Elgavish, Shift reagents and NMR of paramagnetic lanthanide complexes 483
- 39. J. Reuben, Bioinorganic chemistry: lanthanides as probes in systems of biological interest 515
- 40. T.J. Haley, *Toxicity* 553 Subject index 587

VOLUME 5

1982, 1st repr. 1984; ISBN 0-444-86375-3

- 41. M. Gasgnier, Rare earth alloys and compounds as thin films 1
- 42. E. Gratz and M.J. Zuckermann, Transport properties (electrical resitivity, thermoelectric power and thermal conductivity) of rare earth intermetallic compounds 117
- 43. F.P. Netzer and E. Bertel, Adsorption and catalysis on rare earth surfaces 217
- 44. C. Boulesteix, Defects and phase transformation near room temperature in rare earth sesquioxides 321
- 45. O. Greis and J.M. Haschke, Rare earth fluorides 387
- 46. C.A. Morrison and R.P. Leavitt, Spectroscopic properties of triply ionized lanthanides in transparent host crystals 461

Subject index 693

VOLUME 6

1984; ISBN 0-444-86592-6

- 47. K.H.J. Buschow, Hydrogen absorption in intermetallic compounds 1
- 48. E. Parthé and B. Chabot, Crystal structures and crystal chemistry of ternary rare earth-transition metal borides, silicides and homologues 113
- 49. P. Rogl, Phase equilibria in ternary and higher order systems with rare earth elements and boron 335
- H.B. Kagan and J.L. Namy, Preparation of divalent ytterbium and samarium derivatives and their use in organic chemistry 525 Subject index 567

VOLUME 7

1984; ISBN 0-444-86851-8

- 51. P. Rogl, Phase equilibria in ternary and higher order systems with rare earth elements and silicon 1
- 52. K.H.J. Buschow, Amorphous alloys 265
- 53. H. Schumann and W. Genthe, Organometallic compounds of the rare earths 446 Subject index 573

CONTENTS OF VOLUMES 1-21

VOLUME 8

1986; ISBN 0-444-86971-9

- 54. K.A. Gschneidner Jr and F.W. Calderwood, Intra rare earth binary alloys: phase relationships, lattice parameters and systematics 1
- 55. X. Gao, Polarographic analysis of the rare earths 163
- 56. M. Leskelä and L. Niinistö, Inorganic complex compounds I 203
- J.R. Long, Implications in organic synthesis 335 Errata 375 Subject index 379

VOLUME 9

1987; ISBN 0-444-87045-8

- 58. R. Reisfeld and C.K. Jørgensen, Excited state phenomena in vitreous materials 1
- 59. L. Niinistö and M. Leskelä, Inorganic complex compounds II 91
- 60. J.-C.G. Bünzli, Complexes with synthetic ionophores 321
- Zhiquan Shen and Jun Ouyang, Rare earth coordination catalysis in stereospecific polymerization 395 Errata 429 Subject index 431

VOLUME 10: High energy spectroscopy

1988; ISBN 0-444-87063-6

- 62. Y. Baer and W.-D. Schneider, High-energy spectroscopy of lanthanide materials An overview 1
- 63. M. Campagna and F.U. Hillebrecht, *f-electron hybridization and dynamical screening of core holes in intermetallic compounds* 75
- 64. O. Gunnarsson and K. Schönhammer, Many-body formulation of spectra of mixed valence systems 103
- 65. A.J. Freeman, B.I. Min and M.R. Norman, Local density supercell theory of photoemission and inverse photoemission spectra 165
- 66. D.W. Lynch and J.H. Weaver, Photoemission of Ce and its compounds 231
- 67. S. Hüfner, Photoemission in chalcogenides 301
- 68. J.F. Herbst and J.W. Wilkins, Calculation of 4f excitation energies in the metals and relevance to mixed valence systems 321
- 69. B. Johansson and N. Mårtensson, Thermodynamic aspects of 4f levels in metals and compounds 361
- F.U. Hillebrecht and M. Campagna, Bremsstrahlung isochromat spectroscopy of alloys and mixed valent compounds 425
- 71. J. Röhler, X-ray absorption and emission spectra 453
- 72. F.P. Netzer and J.A.D. Matthew, *Inelastic electron scattering measurements* 547 Subject index 601

VOLUME 11: Two-hundred-year impact of rare earths on science

1988; ISBN 0-444-87080-6

H.J. Svec, Prologue 1

- 73. F. Szabadváry, The history of the discovery and separation of the rare earths 33
- 74. B.R. Judd, Atomic theory and optical spectroscopy 81
- 75. C.K. Jørgensen, Influence of rare earths on chemical understanding and classification 197
- 76. J.J. Rhyne, Highlights from the exotic phenomena of lanthanide magnetism 293
- 77. B. Bleaney, Magnetic resonance spectroscopy and hyperfine interactions 323
- 78. K.A. Gschneidner Jr and A.H. Daane, Physical metallurgy 409
- 79. S.R. Taylor and S.M. McLennan, The significance of the rare earths in geochemistry and cosmochemistry 485 Errata 579 Subject index 581

CONTENTS OF VOLUMES 1-21

VOLUME 12

1989; ISBN 0-444-87105-5

- 80. J.S. Abell, Preparation and crystal growth of rare earth elements and intermetallic compounds
- 81. Z. Fisk and J.P. Remeika, Growth of single crystals from molten metal fluxes 53
- 82. E. Burzo and H.R. Kirchmayr, *Physical properties of* $R_2Fe_{14}B$ -based alloys 71
- 83. A. Szytuła and J. Leciejewicz, Magnetic properties of ternary intermetallic compounds of the RT_2X_2 type 133
- 84. H. Maletta and W. Zinn, Spin glasses 213
- 85. J. van Zytveld, Liquid metals and alloys 357
- 86. M.S. Chandrasekharaiah and K.A. Gingerich, Thermodynamic properties of gaseous species 409
- 87. W.M. Yen, *Laser spectroscopy* 433 Subject index 479

VOLUME 13

1990; ISBN 0-444-88547-1

- 88. E.I. Gladyshevsky, O.I. Bodak and V.K. Pecharsky, *Phase equilibria and crystal chemistry in ternary rare* earth systems with metallic elements 1
- 89. A.A. Eliseev and G.M. Kuzmichyeva, Phase equilibrium and crystal chemistry in ternary rare earth systems with chalcogenide elements 191
- 90. N. Kimizuka, E. Takayama-Muromachi and K. Siratori, The systems R2O3-M2O3-MO 283
- 91. R.S. Houk, Elemental analysis by atomic emission and mass spectrometry with inductively coupled plasmas 385
- P.H. Brown, A.H. Rathjen, R.D. Graham and D.E. Tribe, *Rare earth elements in biological systems* 423 Errata 453 Subject index 455

VOLUME 14

1991; ISBN 0-444-88743-1

- 93. R. Osborn, S.W. Lovesey, A.D. Taylor and E. Balcar, Intermultiplet transitions using neutron spectroscopy 1
- 94. E. Dormann, NMR in intermetallic compounds 63
- 95. E. Zirngiebl and G. Güntherodt, Light scattering in intermetallic compounds 163
- 96. P. Thalmeier and B. Lüthi, The electron-phonon interaction in intermetallic compounds 225
- 97. N. Grewe and F. Steglich, *Heavy fermions* 343 Subject index 475

VOLUME 15

1991; ISBN 0-444-88966-3

- 98. J.G. Sereni, Low-temperature behaviour of cerium compounds 1
- 99. G.-y. Adachi, N. Imanaka and Zhang Fuzhong, Rare earth carbides 61
- 100. A. Simon, Hj. Mattausch, G.J. Miller, W. Bauhofer and R.K. Kremer, Metal-rich halides 191
- 101. R.M. Almeida, Fluoride glasses 287
- K.L. Nash and J.C. Sullivan, Kinetics of complexation and redox reactions of the lanthanides in aqueous solutions 347
- 103. E.N. Rizkalla and G.R. Choppin, Hydration and hydrolysis of lanthanides 393
- L.M. Vallarino, Macrocycle complexes of the lanthanide(III) yttrium(III) and dioxouranium(VI) ions from metal-templated syntheses 443
 Errata 513
 Subject index 515

MASTER INDEX, Vols. 1-15

1993; ISBN 0-444-89965-0

VOLUME 16

1993; ISBN 0-444-89782-8

- 105. M. Loewenhaupt and K.H. Fischer, Valence-fluctuation and heavy-fermion 4f systems 1
- 106. I.A. Smirnov and V.S. Oskotski, Thermal conductivity of rare earth compounds 107
- 107. M.A. Subramanian and A.W. Sleight, Rare earths pyrochlores 225
- 108. R. Miyawaki and I. Nakai, Crystal structures of rare earth minerals 249
- 109. D.R. Chopra, Appearance potential spectroscopy of lanthanides and their intermetallics 519 Author index 547 Subject index 579

VOLUME 17: Lanthanides/Actinides: Physics - I

1993; ISBN 0-444-81502-3

- M.R. Norman and D.D. Koelling, Electronic structure, Fermi surfaces, and superconductivity in f electron metals 1
- 111. S.H. Liu, Phenomenological approach to heavy-fermion systems 87
- 112. B. Johansson and M.S.S. Brooks, Theory of cohesion in rare earths and actinides 149
- 113. U. Benedict and W.B. Holzapfel, High-pressure studies Structural aspects 245
- 114. O. Vogt and K. Mattenberger, Magnetic measurements on rare earth and actinide monophictides and monochalcogenides 301
- 115. J.M. Fournier and E. Gratz, Transport properties of rare earth and actinide intermetallics 409
- W. Potzel, G.M. Kalvius and J. Gal, Mössbauer studies on electronic structure of intermetallic compounds 539
- 117. G.H. Lander, Neutron elastic scattering from actinides and anomalous lanthanides 635
 Author index 711
 Subject index 753

VOLUME 18: Lanthanides/Actinides: Chemistry

1994; ISBN 0-444-81724-7

- 118. G.T. Seaborg, Origin of the actinide concept 1
- K. Balasubramanian, Relativistic effects and electronic structure of lanthanide and actinide molecules 29
- 120. J.V. Beitz, Similarities and differences in trivalent lanthanide- and actinide-ion solution absorption spectra and luminescence studies 159
- 121. K.L. Nash, Separation chemistry for lanthanides and trivalent actinides 197
- 122. L.R. Morss, Comparative thermochemical and oxidation-reduction properties of lanthanides and actinides 239
- 123. J.W. Ward and J.M. Haschke, Comparison of 4f and 5f element hydride properties 293
- 124. H.A. Eick, Lanthanide and actinide halides 365
- 125. R.G. Haire and L. Eyring, Comparisons of the binary oxides 413
- 126. S.A. Kinkead, K.D. Abney and T.A. O'Donnell, *f-element speciation in strongly acidic media: lanthanide* and mid-actinide metals, oxides, fluorides and oxide fluorides in superacids 507
- 127. E.N. Rizkalla and G.R. Choppin, Lanthanides and actinides hydration and hydrolysis 529
- 128. G.R. Choppin and E.N. Rizkalla, Solution chemistry of actinides and lanthanides 559
- 129. J.R. Duffield, D.M. Taylor and D.R. Williams, *The biochemistry of the f-elements* 591
 Author index 623
 Subject index 659

VOLUME 19: Lanthanides/Actinides: Physics - II

1994; ISBN 0-444-82015-9

- 130. E. Holland-Moritz and G.H. Lander, Neutron inelastic scattering from actinides and anomalous lanthanides 1
- G. Aeppli and C. Broholm, Magnetic correlations in heavy-fermion systems: neutron scattering from single crystals 123
- 132. P. Wachter, Intermediate valence and heavy fermions 177
- J.D. Thompson and J.M. Lawrence, High pressure studies Physical properties of anomalous Ce, Yb and U compounds 383
- 134. C. Colinet and A. Pasturel, *Thermodynamic properties of metallic systems* 479
 Author index 649
 Subject index 693

VOLUME 20

1995; ISBN 0-444-82014-0

- 135. Y. Ōnuki and A. Hasegawa, Fermi surfaces of intermetallic compounds 1
- M. Gasgnier, The intricate world of rare earth thin films: metals, alloys, intermetallics, chemical compounds, ... 105
- 137. P. Vajda, Hydrogen in rare-earth metals, including RH_{2+x} phases 207
- D. Gignoux and D. Schmitt, Magnetic properties of intermetallic compounds 293 Author index 425 Subject index 457

VOLUME 21

1995; ISBN 0-444-82178-3

- 139. R.G. Bautista, Separation chemistry 1
- 140. B.W. Hinton, Corrosion prevention and control 29
- 141. N.E. Ryan, High-temperature corrosion protection 93
- 142. T. Sakai, M. Matsuoka and C. Iwakura, Rare earth intermetallics for metal-hydrogen batteries 133
- 143. G.-y. Adachi and N. Imanaka, Chemical sensors 179
- 144. D. Garcia and M. Faucher, Crystal field in non-metallic (rare earth) compounds 263
- 145. J.-C.G. Bünzli and A. Milicic-Tang, Solvation and anion interaction in organic solvents 305
- 146. V. Bhagavathy, T. Prasada Rao and A.D. Damodaran, Trace determination of lanthanides in high-purity rare-earth oxides 367 Author index 385
 - Author index 385 Subject index 411

Handbook on the Physics and Chemistry of Rare Earths Vol. 22 edited by K.A. Gschneidner, Jr. and L. Eyring © 1996 Elsevier Science B.V. All rights reserved

Chapter 147

SYNTHESIS AND PROPERTIES OF SINGLE-CRYSTAL NANOSTRUCTURES

C.P. FLYNN and M.B. SALAMON

Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, IL 61801-3080, USA

Contents

	List	of symbols	1
1.	Intro	oduction	3
2.	Basi	c properties of lanthanide metals	7
	2.1.	Exchange mechanisms	7
	2.2.	Magnetic structures	10
	2.3.	Magnetoelastic effects and turn angles	13
3.	Epit	axial growth of rare earth systems	14
	3.1.	Growth of (0001) hexagonal metals on	
		sapphire	15
	3.2.	Other orientations of hcp lattices on	
		sapphire	17
	3.3.	Other substrates	17
	3.4.	Tilted films	19
4.	Mag	netism of epitaxial rare-earth crystals	19
	4.1.	Epitaxial crystal regime	20
		4.1.1. Gadolinium	20
		4.1.2. Dysprosium	21
		4.1.3. Erbium	24
		4.1.4. Other systems	25
	4.2.	The thick-film limit	25
		4.2.1. Strain relaxation	26
		4.2.2. Effect on the phase diagram	27
		4.2.3. Effects on the magnetic state	30
	4.3.	The thin-film limit	32

		4.3.1. Gadolinium	34
		4.3.2. Other lanthanides	36
	5.	Superlattices	39
		5.1. Magnetic scattering from superlattices	40
		5.2. Superlattice ordering	46
		5.2.1. <i>c</i> -axis samples	47
		5.2.1.1. Gd/Y superlattices	47
		5.2.1.2. Dy/Y superlattices	48
		5.2.1.3. Ho/Y superlattices	54
		5.2.1.4. Er/Y superlattices	54
,		5.2.1.5. Lu-based superlattices	59
'		5.2.1.6. Other superlattice	
)		structures	65
		5.2.2. a- and b-axis samples	66
)		5.2.2.1. a -axis and b -axis Dy/Y	66
)		5.2.2.2. b-axis Gd/Y	68
		5.3. Interlayer coupling and long-range	
ļ		coherence	69
;	6.	Conclusions	71
;		Acknowledgements	73
5		Appendix: Self-energy and pair interactions	
r		in linear response	73
)		References	76

List of symbols

Ь	boundary energy parameter	$b_{\rm R}$, $b_{\rm A}$	nuclear scattering length of lanthanide
b	Burgers' vector		and non-magnetic element, respectively
$B_{\rm eff}(r)$	effective magnetic field at a lanthanide	bcc	body centered cubic
_	site	CAM	c-axis modulated magnetic structure
B _j	magnetization peaks at lock-in transitions	a*, b*, c*	reciprocal lattice vectors

C _R	lattice spacing of lanthanide R in the growth direction
C _A	lattice spacing of non-magnetic species A in the growth direction
с , с	c-axis lattice vector and its magnitude
C _{ij}	elastic constants
d, d_{c}	domain size; its critical value
dhcp	double hexagonal close packed
$E_{\rm F}$	Fermi energy
$E_{\rm me}, \Delta E_{\rm me}$	magnetoelastic energy; change in magnetoelastic energy
Es	strain energy
Ei	self-energies
$E_{\mathfrak{t}}$	total energy
<i>E</i> ₁₂	interaction energy
$F(\kappa), F_{\rm R}(\kappa)$	magnetic form factor; form factor for lanthanide atom
FC	field cooled
fcc	face centered cubic
$F(q/2k_{\rm F})$	Lindhard function
G	reciprocal lattice vector
g,	Landé g-factor
hcp	hexagonal close packed
H _c	critical field to produce ferromagnetic alignment
H _r	anisotropy field in a random anisotropy model
H _s	saturation magnetic field
$H_{\rm ex}$	exchange field in a random anisotropy model
$I_{\rm nuc}(\kappa)$	nuclear scattering intensity
$\mathcal{J}(\boldsymbol{R}); \ \mathcal{J}(\boldsymbol{q})$	the exchange interaction, and its Fourier transform
$J_{ij}^{lpha\!eta}$	exchange interaction between atom <i>i</i> in block α and atom <i>j</i> in block $\beta j_{sf}(\mathbf{r}-\mathbf{R}_i)$,
j _{sf} (q)	s-f exchange interaction on lanthanide atom at R_i and its Fourier transform
$\langle \boldsymbol{J}_{\mathrm{R}} \rangle, \langle \boldsymbol{J}_{\mathrm{z}}^{\mathrm{R}} \rangle$	average angular momentum of lanthanide R
$J_{\rm i}, J(q)$	total angular momentum of lanthanide atom at R_i , and its Fourier transform
$J_{ m af}$	effective antiferromagnetic exchange in transition-metal superlattices

<i>J</i> ₀ , <i>J</i> ₁	exchange interactions for nearest neighbors on the same and adjacent planes
J_2	exchange interaction for next-nearest neighbor planes
K_i, \hat{K}	magnetoelastic coupling constants
k _F	Fermi wavevector
$k_{\rm F\parallel}^{\rm A}, k_{\rm F\perp}^{\rm A}$	Fermi wavevectors in metal A parallel and normal to an interface
1	domain size
MBE	molecular beam epitaxy
$M(\kappa)$	Fourier component of magnetization
ML	monolayer
Ν	total number of atomic planes in a bilayer
N _R	number of lanthanide planes in a bilayer; R can be a chemical symbol
N _A	number of non-magnetic planes in a bilayer; A can be a chemical symbol
N _m	number of bilayers contributing coherently to the magnetic neutron intensity
Q	wave vector of an incommensurate magnetic phase (fraction of τ)
Q_{R}, Q_{eff}	lanthanide and effective superlattice magnetic wavevectors, respectively
<i>q</i> , <i>q</i> _i	charge
r	position
rem	remanent magnetization
RHEED	reflection high energy electron diffraction
RKKY	Ruderman–Kittel–Kasuya–Yosida interaction
r_0	classical radius of the electron
s, s(r)	conduction electron spin and spin density
\boldsymbol{S}_i	spin on lanthanide atom at position R_i
$S_{\rm mag}^{\pm}(\kappa)$	structure factor for $\pm Q_R$ magnetic satellites
$S_{\rm nuc}(\kappa)$	nuclear structure factor
$T_{\rm C}$	Curie temperature
T _N	Néel temperature
T _p	onset temperature for random anisotropy order in a thin film
<i>t</i> , <i>t</i> _c	layer or film thickness, critical film thickness

v_0	unit cell volume	κ _D	Debye-Hückel screening parameter
v, V	electrostatic potentials	$\Delta \kappa_{ m obs,mag,nuc}$	observed, nuclear and magnetic widths
W	Debye-Waller factor		of neutron diffraction lines
W_{\min}, W_{t}	minimum, total domain energy	Λ	superlattice period
x	position	$\mu_{ m B}$	Bohr magneton
$x_i(\mathbf{r})$	perturbations	ξ	effective de Gennes factor
ZFC	zero field cooled	ξm	magnetic coherence length
β	constant; exponent of magnetization	ρ	density of states
Г	de Gennes factor	$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{el}}$	magnetic contribution to the elastic
γ	neutron gyromagnetic ratio; attenuation		neutron scattering cross section
	factor in diffusion model	τ, τ	magnetic wavevector in reciprocal
δ	critical exponent		lattice units; its magnitude
$\varepsilon, \varepsilon_0$	strain, minimized or clamped strain	$\Phi, \Phi(j)$	phase advance of the magnetization
ϵ	dielectric constant	(-)	wave across a bilayer, its value at j
ζ	arbitrary fraction of a reciprocal lattice	$\chi(\mathbf{r}-\mathbf{R}_i)$	local susceptibility of the conduction
	unit		
κ , κ _α , κ	scattered wave vector, its alpha component, unit vector	ω	plane

1. Introduction

The first rare-earth superlattices were grown in the mid-1980s by J. Kwo at Bell Laboratories (Kwo et al. 1985b) on substrates of Nb grown on sapphire prepared at the University of Illinois at Urbana/Champaign (Durbin et al. 1982). The broad synthesis pathway leading from sapphire to all manner of ceramic, metallic, and intermetallic materials, of which this rare-earth growth forms a part, is to be described elsewhere (Yang and Flynn 1995). In less than a decade, the synthesis and study of rare-earth superlattice stacks (Kwo et al. 1985a,b, Salamon et al. 1986) has developed a significant degree of precision, reproduced among several groups worldwide. As yet, however, it cannot rival the much greater stream of research on semiconductors. Epitaxial growth of rare-earth systems in various orientations is described in sect. 3 of this review.

The rare earths provide beautiful model systems with which the basic principles of magnetic thin-film systems may be explored. At the time of writing, the bare bones of the subject are just becoming visible (Majkrzak et al. 1991, Salamon et al. 1991). In that sense, the present review is premature. In undertaking this review, therefore, the authors had two goals in mind: first to describe the progress to date in the study of epitaxial rare earths in general and their superlattices in particular; and second, to clarify principles common to all thin-film magnetic systems. It is our hope that this larger viewpoint will make the review more widely useful.

This introductory section has the purpose of reviewing a simple framework in which the properties of epitaxial systems may be understood. An important factor is the magnetostriction and strain dependence of magnetism generally exhibited by the rare earths. As bulk materials, the rare earths mainly adopt the hcp lattice structure and, in metallic and alloy form, display elegant and complex magnetic structures (Elliott 1972, Coqblin 1977, Jensen and Mackintosh 1991). The low-temperature phase of many of these elements has a ferromagnetic component. The intermediate phases (except for Gd) are oscillatory, and are truly characteristic of the lanthanide metals. For reasons related to Fermi surface topology, and described in sect. 2, the spatial oscillations of magnetism in the heavy lanthanides Tb through Tm typically occur along the *c*-axis of the hcp structure, with wavelengths > 20 Å (7 or more lattice planes). This behavior is well illustrated by Dy, which is paramagnetic above its Néel temperature $T_N = 185$ K. Between T_N and the Curie temperature $T_C = 85$ K, there exists helimagnetic order in which the moments in each basal plane align in the plane, but with the moments of successive planes rotated progressively by 30° to form a spiral along *c*. At low temperatures, an orthorhombic distortion occurs as ferromagnetic order sets in along one unique (elongated) *a*-axis.

Our first purpose is to understand the changes that take place when the rare-earth metal is part of a multilayer structure in which successive layers are formed from different metals with each layer only nanometers thick. Despite the complexity of many lanthanide phases, it is a fact that these materials remain magnetically robust as components of a multilayer stack. Each block of lanthanide metal retains a well defined magnetic phase diagram in which the material transforms from one phase to another at particular values of temperature, applied magnetic field, and lattice strain. For reasons described below, the specification of the state requires the complete elastic strain tensor, or otherwise the atomic volume and shape. This robustness of the magnetic material must derive from the fact that the lanthanide moments take essentially fixed values, and that the correlations among them in a multilayer remain long-ranged in at least one of the space dimensions. There are far-reaching consequences of this simplified behavior. The practical result is that the magnetic structure of a multilayer stack, to zeroth approximation, may be obtained by assigning to each layer a magnetic structure identical to that of the bulk material at the same temperature, field, and state of strain.

The example of a Dy/Y superlattice will clarify this model. Y is a nonmagnetic rareearth metal and Dy, as specified above, is helimagnetic below 185 K and ferromagnetic below 85 K. From the model outlined above we therefore anticipate that a Dy/Y superlattice at 100 K consists of non-magnetic Y separating helimagnetic Dy blocks with approximately the same wavelength as the bulk. This is in fact observed to be the case. Two points of particular importance must be flagged here if the model is to be employed in a useful way. First, the helimagnetic wavelength is *not* precisely that of the bulk at the same temperature; nor does the ferromagnetic transition occur at 85 K in the superlattice (it is in fact completely suppressed). It turns out that the changes arise because there is epitaxial strain present in the multilayer, and this causes the material to differ from the freestanding bulk. These differences of behavior then find a natural explanation from the model as consequences of the state of strain within the lanthanide blocks. Epitaxial thinfilm effects of this type are the subject matter of sect. 4 of the review. The second point of special interest is that long-range magnetic order is observed to propagate coherently from one magnetic Dy layer to the next *through the non-magnetic Y spacer material*. This new behavior finds no explanation in terms of successive magnetically robust blocks. Instead, the observed coupling among layers is a true superlattice effect that reflects properties of the composite structure, rather than those of its component blocks. Sect. 5 of the review contains information on interaction effects of this type.

The robust nature and interesting variety of lanthanide magnetic phases follow from the particular character of the lanthanide atoms. It is well known that the magnetic moments derive principally from 4f electrons that lie deep within the atom, leaving the solid-state electronic structure and binding to the three $6s^26p$ (or 5d) outer electrons. With the inner $4f^n$ electrons obeying Hund's rules, the magnetic behavior is largely determined by n. This simple prescription is significantly broken only by subshell filling anomalies for Eu (n=6) and Yb (n=13). The spin S and orbital momentum L of the 4f shell can, in addition, be excited to states of total angular momentum J that have higher energies than that of the Hund's rule ground state. Because the energy splittings are generally much larger than the values of $k_{\rm B}T$ relevant to magnetically ordered phases, these core excitations do not have much influence on magnetism of the heavy lanthanides. The case of light lanthanides is different, and excited states figure prominently in their behavior because of the inverted L-S multiplet states. While the investigation of their superlattices has scarcely yet begun, some comment on light lanthanide superlattices is included in sect. 5.

When these anisotropic lanthanide atoms are placed on crystal lattice sites of an hcp metal, the "crystal field" interactions confine the core magnetic moments to certain easy directions (or planes). Because of the compactness of the 4f core, there is virtually no direct overlap leading to direct exchange interactions among the atoms. Instead, the strong magnetic interaction is the indirect exchange interaction caused by induced polarizations of the conduction electrons by the 4f cores. While oscillatory in form along c, the indirect exchange greatly exceeds the dipolar interaction in its effect upon the magnetic phase diagram. The magnetic phases of the lanthanides are thus largely determined by a competition between indirect exchange and terms of the crystal field interaction, as modified by temperature, strain, and magnetic fields.

Because the crystal field figures prominently in determining their magnetic structure, lanthanides are highly strain sensitive. Epitaxy in tailored multilayered systems causes strain as a consequence of pseudomorphic growth. The lanthanides and their Column-IIIB analogs have lattice constants that differ by a few percent across the series. Thus, when grown in atomic registry, lanthanide stacks automatically occur with strains at the 1% level. These strains are large enough to cause dramatic changes of magnetic phase diagram. Thus, for example, a ferromagnetic phase of Dy that occurs in equilibrium in the unstrained bulk may become completely inaccessible in a constrained epitaxial system. In sect. 4 we describe examples of precisely this behavior for epitaxial films of Dy and Er on Y. It is worth stating explicitly that since all one-dimensional solutions of the elasticity equations are uniform, the atomic spacings must remain uniform through the thickness of any undislocated thin film. Anelastic response, including interfacial slip and dislocation processes, may, of course, relieve the constraints. In sect. 4 we describe the consequences of these effects in terms of an "epitaxial phase diagram". The central point, worth reiterating here, is that the magnetic structures of epitaxial films adopt forms appropriate to *the existing state of strain*.

Section 2 describes characteristic spin structures of the lanthanide metals that originate almost exclusively from the polarization of the conduction band electrons by the atomic moments of the cores. This is typically described by a Heisenberg-like interaction between two lanthanide atoms, say i and j, with the exchange interaction J_{ii} an oscillatory function of the distance between i and j. As described in the Appendix, the interaction arises in linear response theory entirely from the spin density disturbance caused by a scatterer, and its functional dependence on distance conforms to that of the disturbance. Often it is convenient to employ the Fourier transform J(q) of the exchange interaction. The Fermi surface of trivalent rare-earth metals is characterized by nearly parallel sheets of nesting structures that make the electron liquid almost unstable to the formation of a spin-density wave. The spanning wavevector Q that connects these sheets and maximizes J(q) thereby fixes the direction and periodicity of the observed spin structure. The *polarization* of the magnetization wave is separately determined by the spin orientations permitted by the crystal field, as also are details of the actual spin structure (Gibbs et al. 1986, 1988, Isaacs et al. 1989). In the hcp lattice for trivalent lanthanides, J(q) peaks sharply as q is varied through Q, parallel to c. In the orthogonal directions, however, the coupling is believed to undergo a featureless decay on a length scale governed by the inverse of the 4f-core radius.

We hasten to mention that the degree to which this elegant description attains quantitative validity in practice remains in doubt. As soon as long-range order is established, the magnetization wave must induce gaps at the Fermi surface (and higher order gaps below) and modifies both the response and the interactions. While these effects may in principle be described by higher orders of perturbation theory (Elliott and Wedgwood 1964) it has never been demonstrated that the real complexities do not invalidate the simple formulation. Indeed, efforts to explain the temperature-dependent helimagnetic pitch by the three-layer model (Elliott 1972) produce strongly temperaturedependent values for the exchange energies, for which the opening of superzone gaps provides one plausible explanation.

Response and interactions in multilayers may be treated within the same formalism of linear response theory but with a response function that is now dependent on both source and test positions. The exchange energies $J_{ij}^{\alpha\alpha}$ that couple two atoms within the same block α differ from those connecting analogous atoms of the bulk material. The sums over all pairs that represent the total energies in the two cases differ in two ways. First, certain terms in the energy for the bulk are missing for sites that lie outside block α of the superlattice, and are replaced in the sum by terms that involve the second component of the superlattice. Also, the coefficients themselves derive from the band structure, and are thus inevitably modified near boundaries. At the simplest level, the pitch of a helimagnetic spiral may be expected to change as an interface is approached. A more extreme possibility is that the superlattice band structure could evolve with very different nesting features, and consequently with strongly modified exchange coefficients. The fact that observed magnetic behavior is robust against these types of perturbation must indicate that short-range terms dominate the magnetic energy. No explicit demonstration from theory that terms connecting more remote pairs are negligible is, as yet, available.

Great interest attaches to additional exchange coefficients $J_{ij}^{\alpha\alpha'}$ that connect moments in *different* blocks α and α' . These are not contained in any simple model. They represent terms of considerable significance in this review as they can be responsible for the existence and character of long-range magnetic order in superlattices. Section 5 describes available results in this area. A conceptually simple approach to their calculation is to solve the band structure for the superlattice first, and then derive the coupling energy as a pairwise sum over core interactions, just as in bulk systems. Such calculations are only now emerging. Questions of the change of band structure associated with magnetic order again pass beyond a linear response framework. At the present level of understanding, the polarization induced by lanthanide planes (or pairs of planes), embedded in a block of the intervening material, is used to estimate the interblock coupling coefficients (Yafet 1987a, Yafet et al. 1988). We return to this subject in sect. 6.

2. Basic properties of lanthanide metals

2.1. Exchange mechanisms

The complex magnetic structures of the lanthanide elements and their alloys derive from the interplay of band structure, crystal field, lattice strain, and the Hund's rule ground states of the lanthanide atoms, as noted in sect. 1. Progress at various stages over the years has been summarized in successive volumes by Elliott (1972), by Coqblin (1977), and by Jensen and Mackintosh (1991). Here we review only those most important aspects of lanthanide bulk magnetism required to prepare the reader for the new aspects introduced by epitaxial strain, clamping to a substrate, and the ability to separate magnetic atoms by non-magnetic layers. These consequences of epitaxial growth of superlattices have in turn provided new avenues for exploring lanthanide magnetism.

The indirect exchange interaction arises from the polarization of the conduction electrons by the localized 4f moment, through the Heisenberg interaction (Freeman 1972). The Hamiltonian that describes the situation between the core and the conduction states is

$$H = -\int d^3r j_{\rm sf}(\mathbf{r} - \mathbf{R}_i) s(\mathbf{r}) \cdot \mathbf{S}_i, \qquad (1)$$

where s(r) is the conduction electron spin density, and S_i the lanthanide spin. Because the spin-orbit energy is large, it is convenient to write the exchange interaction in terms of the total angular momentum $J_i = S_i/(g_1 - 1)$, with g_1 the Landé g-factor. A full treatment of the interaction between two lanthanide atoms in second-order perturbation theory is

given in the Appendix. A heuristic argument will serve our present purposes here. The lanthanide ion acts as an effective point magnetic field,

$$B_{\rm eff}(\mathbf{r}) = \frac{V j_{\rm sf} \,\delta(\mathbf{r} - \mathbf{R}_i)(g_{\rm J} - 1) \,\mathbf{J}_{\rm i}}{g \mu_{\rm B}},$$

and generates a magnetization cloud in the conduction electrons given approximately by

$$M(\mathbf{r}) = j_{\rm sf} \, \chi_{\rm el}(\mathbf{r} - \mathbf{R}_i) \frac{(g_{\rm J} - 1) J_i}{g \mu_{\rm B}},\tag{2}$$

where $\chi_{el}(\mathbf{r}-\mathbf{R}_i)$ is the non-local susceptibility of the conduction electrons. This induced polarization is the magnetic analog of Friedel oscillations. A second lanthanide atom at \mathbf{R}_j interacts with the induced spin polarization via eq. (1), leading to an interaction energy between the two atoms given by

$$E_{ij} = 2j_{\rm sf}^2 \,\chi_{\rm el}(\boldsymbol{R}_j - \boldsymbol{R}_i) \frac{(\boldsymbol{g}_{\rm J} - 1)^2 \boldsymbol{J}_i \cdot \boldsymbol{J}_j}{g^2 \mu_{\rm B}^2}.$$
(3)

In second-order perturbation theory the total interaction energy is just the sum over all pairs of pairwise energies having the form of eq. (3).

In a concentrated system of N spins, it is often more convenient to treat Fourier components of the total angular momentum; these are given by

$$J(q) = \frac{1}{N} \sum_{i} J_{i} \exp(iq \cdot R_{i}).$$
(4)

By summing E_{ii} over all pairs we find an effective Hamiltonian

$$H_{\text{eff}} = -\sum_{q} \mathcal{J}(q) J(q) \cdot J(-q), \qquad (5)$$

where

$$\mathcal{J}(\boldsymbol{q}) = \frac{V}{2g^2 \mu_{\rm B}^2} (g_{\rm J} - 1)^2 j_{\rm sf}^2 \,\chi_{\rm el}(\boldsymbol{q}),\tag{6}$$

and $\chi_{el}(q)$ is the wavevector-dependent susceptibility of the conduction electrons. In a metal with a spherical Fermi surface of radius k_F , we have $\chi_{el}(q) = (3N\mu_B^2/VE_F)F(q/2k_F)$, where the Lindhardt function F(x) decreases smoothly from unity at x = 1, with only an inflection at $2k_F$. The magnitude of the exchange interaction is set by $j_{sf}^2 \Gamma/E_F$, where $\Gamma = (g_J - 1)^2 J(J + 1)$ is known as the de Gennes factor (de Gennes 1958).

According to this description, the magnetic ordering of the lanthanide metals is determined by the conduction electron band structure of the solid. These exchange



Fig. 1. Wavevector-dependent susceptibility of the rare-earth IIIB elements. The curves are shifted for clarity by 4 (Y), 2 (Dy), 0 (Lu), -2 (Er) and -8 (Gd) states/Ryd atom. Note that the Y susceptibility has been divided by two. Also shown is the 4f form factor for Gd relative to its value at q=0.

energies for simple metals are termed the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions; for the lanthanides, however, the Fermi surfaces remain similar to each other but are far from simple (Freeman 1972). The transition temperature from the disordered to the ordered state is determined by the largest value of the indirect exchange interaction. In mean-field theory this is given (Jensen and Mackintosh 1991) by

$$T_{\rm c} = \frac{NJ(J+1)}{3k_{\rm B}} \mathcal{J}(\boldsymbol{\varrho}) \propto \Gamma, \tag{7}$$

where Q is the value of q that maximizes $\mathcal{J}(q)$. Thus Q is completely determined by the conduction electron susceptibility. A more complete treatment must take into account the actual structure of $j_{sf}(r)$. The compact size of the 4f cores nevertheless guarantees that the Fourier transform is broad and relatively featureless, so that corrections for core structure are small.

The indirect exchange interaction was first calculated from the band structures of the heavy rare earths by Evenson and Liu (1968). Figure 1 shows the susceptibilities of Y, Dy, Lu, Er, and Gd (Liu et al. 1971); each is shifted relative to Lu as described in the caption. Also shown is the form factor $[j_{sf}(q)/j_{sf}(0)]$. When multiplied by the square of the form factor the $q \neq 0$ peak is suppressed for Gd and the maximum for Dy shifts to a point approximately 60% of the distance to the zone boundary (i.e. $Q_z = 0.6 \pi/c$, with c the hexagonal lattice constant of Dy). No strong features are apparent in other regions of the Brillouin zone. Note that the magnetic response functions of the conduction electrons in non-magnetic Y and Lu are quite similar to those of the magnetic lanthanide elements; indeed Y exhibits a stronger response than any of the 4f elements.

The periodicity Q is often expressed in terms of an effective phase advance per lattice plane, called the turn angle and given by $\omega = (Q_z c/4\pi) \times 360^\circ$ (a factor two in the denominator reflects two atomic planes per hcp unit cell). The turn angle associated with the peak in fig. 1 is 54°/Dy layer, somewhat larger than the observed value (Koehler 1972) of 43°. The exchange energies calculated for the non-magnetic rare earth elements yttrium and lutetium are remarkably similar to that of Dy, and this is apparent also from the observed phase relationships. For example, yttrium alloys with the lanthanides order into modulated structures even when the magnetic component is dilute (Elliott 1972). Thus 0.5 at.% Er, erbium orders in yttrium at 0.2 K into a helical structure with $Q_z = 0.56 \pi/c$ ($\omega = 50.4^{\circ}$) (Caudron et al. 1990). Recent studies of the alloys Dy_xLu_{1-x}, with x = 0.4, 0.5 and 0.6, show that they all order with the turn angle $\omega = 45.7^{\circ}$ (Everitt et al. 1994). If, for binary alloys among the lanthanides and with Y, an effective de Gennes factor is defined as $\xi = c\Gamma_1 + (1-c)\Gamma_2$, with Γ_1 and Γ_2 the de Gennes factors of the constituents, the observed Néel temperatures are predicted accurately by $T_N = 47 \text{ K} \xi^{2/3}$, rather than the linear relation of eq. (7) (Rhyne 1972). The epitaxial alloys follow the same law as bulk samples.

2.2. Magnetic structures

While the nature of the Fermi surface determines the periodicity, the detailed structure of the ordered state is strongly influenced by the presence of the hexagonal crystal field (Kasuya 1966). The most important contributions are the axial components which, if positive, cause the 4f moments to lie in the basal plane of the hexagonal structure as for Tb, Ho and Dy; if negative they induce either ferromagnetic or *c*-axis-modulated order as in Gd and Er. Tb, Ho, and Dy order initially with the magnetic moments in each hexagonal sheet aligned ferromagnetically, and with the total moments of the sheets rotated successively by the turn angle ω . The resultant spiral structure is termed the helimagnetic phase. Er orders with the rare-earth moments in each hexagonal plane aligned with the *c*-axis, but with a magnetization that oscillates sinusoidally. For this case the turn angle measures the phase advance of the oscillation in this *c*-axis modulated (CAM) phase. The magnetic structures are summarized by the sketch in fig. 2.

Neutron scattering has been the main tool used for the study of lanthanide magnetic structures (Koehler 1972), and X-ray scattering has made important recent contributions (Gibbs et al. 1986, 1988, Isaacs et al. 1989). The neutron magnetic moment couples to the total magnetization of each atom. The elastic scattering cross section is written in a compact form as (Squires 1978),

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{el}} = \left(\frac{\gamma_n r_0}{2\mu_\mathrm{B}}\right)^2 \left|\widehat{\kappa} \times \left(\langle \boldsymbol{M}(\kappa) \rangle \times \widehat{\kappa}\right)\right|^2 \tag{8}$$

with γ the neutron gyromagnetic ratio, and r_0 the classical radius of the electron. $M(\kappa)$ is the Fourier component of the total magnetization at the scattering wavevector κ . Note that only components of the magnetization perpendicular to the scattering wavevector



Fig. 2. Magnetic structures of the heavy lanthanide metals (from Coqblin 1977).

contribute to the scattered intensity. In the case of modulated phases like those exhibited by the lanthanides, eq. (8) becomes

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{el}} = (r_0 \gamma_n)^2 \left(\frac{1}{2}g_J F(\boldsymbol{\kappa})\right)^2 \exp(-2W) S_{\mathrm{mag}}^{\pm}(\boldsymbol{\kappa}). \tag{9}$$

Here, the form factor is given by

$$S_{\rm mag}^{\pm}(\boldsymbol{\kappa}) = \frac{(2\pi)^3}{\nu_0} \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \widehat{\boldsymbol{\kappa}}_{\alpha} \cdot \widehat{\boldsymbol{\kappa}}_{\beta} \right) \left\langle \boldsymbol{J}_{\alpha} \right\rangle \left\langle \boldsymbol{J}_{\beta} \right\rangle \sum_{\tau} \frac{1}{4} \left[\delta(\boldsymbol{G} + \boldsymbol{Q} - \boldsymbol{\kappa}) + \delta(\boldsymbol{G} - \boldsymbol{Q} - \boldsymbol{\kappa}) \right]. \tag{10}$$

Each reciprocal lattice point G is bracketed by a pair of magnetic satellites which have non-zero amplitudes provided that the modulated magnetization has a component perpendicular to the scattering wavevector κ . The quantity J_{α} is a component of the angular momentum vector of the atom; $F(\kappa)$, its magnetic form factor; and v_0 , the unit cell volume.

Figure 3 shows several neutron scattering scans of a 400 Å Dy film grown epitaxially on Lu (Beach 1992). The scan is along the c^* -axis in reciprocal space; the peak at $|\tau| = 2.23 \text{ Å}^{-1}$ is the Dy Bragg peak while that at 2.28 Å⁻¹ is the Lu Bragg peak. Magnetic satellites appear below 160 K at positions $\tau \pm 0.22 \text{ Å}^{-1}$. That magnetic satellites occur with κ parallel to Q indicates that the magnetization wave is transverse; further analysis shows it to be helical. By contrast, fig. 4 shows data (Borchers et al. 1991), for a 3950 Å Er film grown on Y, with the scan also along c^* , but with τ now nearly parallel to the b^* -axis. The magnetic satellites observed below 65 K indicate that the magnetization wave is longitudinal and sinusoidally modulated along the *c*-axis. As the temperature is lowered,



Fig. 3. Neutron scattering data for a 400 Å Dy film grown epitaxially on Lu. The peak at 2.23 Å⁻¹ is the (0002) peak of Dy; that at 2.27 is from the Y under-layer. Note the symmetric magnetic satellites surrounding the (0002) peak. The sample is ferromagnetic at and below 95 K.

the changing positions of the magnetic satellites reflect the temperature dependence of the turn angle. For Dy on Lu (as for bulk Dy below 85 K) the helimagnetic structure collapses below 95 K, adding intensity to the Bragg peak. The turn angle is then zero and the sample is ferromagnetic. Dy displays a continuous variation of turn angle with temperature that is described in sect. 4, in the context of epitaxial Dy films. The temperature dependence of the turn angle of Er proceeds through a sequence of discrete values, or lock-in states, which are included in the discussion of Er films in sect. 3.



Fig. 4. Neutron scattering data for a 3950 Å Er film grown epitaxially on Y. The central peak is the $(10\bar{1}0)$ Bragg peak, and the scan is along the c^{\bullet} axis. The additional peaks that appear are higher Fourier components indicating a change from sinusoidal to square-wave modulation.

2.3. Magnetoelastic effects and turn angles

Observed turn angles and magnetic order must reflect the balance among basal-plane anisotropy, changes in the band structure induced by the growth of long-range order and, especially, magnetostrictive effects. The resulting variations of turn angle with temperature may be continuous, as for Dy, or may exhibit discrete "lock-in" steps, as found for Er, Ho, and Tb (Gibbs et al. 1986, 1988, Isaacs et al. 1989). Ho and Tb, with M perpendicular to Q, exhibit discrete steps in Q associated with "spin-slips" (Gibbs et al. 1985, Bates and Cowley 1988). The basal plane moments lie only along easy directions, advancing in steps of 30° per plane, but with missing steps (slips) interspersed. Invariably the trend is for the turn angle to decrease with decreasing temperature, and thus for the density of spin slips to increase. This suggests that the mechanism that favors a ferromagnetic low-temperature phase plays a role in the temperature dependence of the modulation wavelength. Little is currently known about the coherence length and its origins for spin slip structures, either longitudinally along c, or laterally in the basal plane, although scattering linewidths indicate typical transverse length scales ~10³ Å (Gibbs et al. 1991). The energetics of the helix-ferromagnetic transition have been treated in detail for Dy, and have been reviewed by Cooper and by Rhyne (Cooper 1972, Rhyne 1972). Singleion effects due to strain-dependent changes in the crystal field dominate in ferromagnetic Dy, but are ineffective in the helical state. In the ferromagnetic state there is a uniform magnetoelastic distortion that results in a net energy gain termed the "driving energy". At the Curie point of Dy this energy gain exceeds the exchange energy difference between helical and ferromagnetic states; both are approximately 2.2 K/atom at $T_{\rm C}$. The material undergoes an orthorhombic distortion comprising a 0.2% expansion along a, with a 0.5% contraction along b and a 0.3% elongation along c. In the case of Er, the calculation is considerably more subtle because the single-ion terms are the same in the ferromagnetic and CAM phases. However, the two-ion magnetoelastic terms, due to the strain dependence of the exchange energy, are slightly different. The driving energy in this case has been found (Rosen et al. 1973) to be approximately 2 K/atom, much as in Dy. The distortion for Er is primarily a *c*-axis elongation of 0.32%, with smaller *a*- and *b*-axis compressions.

Crystal field effects are relatively weak for Gd because the Gd 4f shell is half-filled, making it a special case. Bulk gadolinium orders as a c-axis ferromagnet, and remains ferromagnetic at lower temperatures. A weak canting transition is spread over a broad temperature range around 226 K, but no helimagnetic order develops (Cable and Wollan 1968, Salamon and Simons 1973). Dipolar interactions overcome the axial anisotropy of Gd in sufficiently thin samples, causing them to order ferromagnetically in the basal plane.

In the magnetoelastic literature, the partial suppression of magnetoelastic distortions in a helical phase has been termed "clamping". This effect is quite different from the clamping that we discuss below, which is the constraint imposed on an epitaxial film by its adhesion to a thick substrate. In sect. 4, we describe the properties of thin rareearth films grown as epitaxial trilayers with nonmagnetic Y, Lu, and their alloys. These epitaxial crystals allow the effects on the magnetic phase diagram of coherency strain to be distinguished from the effects of epitaxial clamping. Section 5 of the review describes the properties of superlattice structures grown to date, in terms of the structures of the epitaxial layers and their coupling through non-magnetic spacers.

3. Epitaxial growth of rare earth systems

The present discussion is directed mainly to hexagonal rare earth systems because none of the cubic lanthanides has as yet been grown by epitaxial methods. Both the hcp structure typical of heavy lanthanides (Kwo et al. 1985a,b, Salamon et al. 1986) and the more elaborate dhcp structure of the light lanthanide Nd (Everitt et al. 1994) have been grown successfully, and without particular effort, since the stable phase of the bulk system seems to reproduce in an epilayer. As in the growth of other metal and ceramic systems, the procedure of choice requires the initial growth of a buffer layer on sapphire, Al_2O_3 , and this buffer provides the active template (Cunningham et al. 1988). Both the buffer

and rare-earth epilayer grow by the step flow mechanism as high quality crystals at a temperature of about $0.35-0.4 T_m$ (Yang and Flynn 1995) for reasons related to surface diffusion (Flynn 1988) that show characteristic differences among metals, salts and covalent crystals (Yang and Flynn 1989). Research on epitaxial rare earths remains in its developmental stages. For this reason, techniques developed for other hexagonal systems have not yet been adapted to rare earths, even though they clearly identify important future avenues for rare-earth superlattice research. The growth opportunities that may follow by adapting procedures pioneered for other hexagonal systems are summarized in the present review.

3.1. Growth of (0001) hexagonal metals on sapphire

Multilayers of Cu and Nb grown by Schuller (Schuller 1980) in the 1980s exhibit spectacular X-ray Bragg scans that clearly arise from interference among successive blocks of Cu (111) and Nb (110), much like interference in earlier semiconductor superlattices (Chang et al. 1973). Unfortunately the tetragonal Nb plane grows on the threefold Cu in three alternative domains with relative 120° orientations, for reasons apparent from the symmetry. Therefore the Cu component of these systems contributes to a three dimensional reciprocal lattice but the Nb, being random, does not. The first metal superlattices of high quality were grown from bcc Ta and Nb by Durbin, Cunningham, Mochel and Flynn (Durbin et al. 1981) using epitaxial grade sapphire substrates. These results establish that (110) Nb and Ta grow on (11 $\overline{2}0$) Al₂O₃ with mosaic spread $\sim 0.1^{\circ}$, still narrower Bragg spots, and a three dimensional reciprocal lattice derived from Nb and Ta blocks with interdiffusion limited to a few interfacial planes at most. The second step, taken by Durbin, Cunningham and Flynn (Durbin et al. 1982), was to grow Nb/Ta superlattices in the three orthogonal orientations (110), (111) and (211), on the three orthogonal surfaces $(11\overline{2}0)$, (0001) and $(1\overline{1}00)$ of sapphire, and in a fourth, (100) orientation, on MgO (100). It was possible to grow these orientations simultaneously on the three Al₂O₃ templates and MgO, which indicates significant isotropy of the growth conditions. The third step was the growth on sapphire (0001) by Cunningham and Flynn (1985) of multilayers and superlattices containing both (111) fcc Ir and (0001) hcp Ru. In all cases the metal diffraction peaks maintained the high quality of the earlier bcc studies. The practical effect of these early efforts is that controlled templates for bcc, fcc and hcp metals became available and, in the case of bcc metals, for several choices of orientation. In addition, these results provided a strong indication that Al₂O₃ could provide a precise and diverse starting point for other pathways of epitaxial synthesis.

Further brief comment on the sapphire to bcc metal epitaxy is warranted. McWhan (1985) pointed out that the three epitaxial pairs given above with their observed alignment of axes, conform to a fixed three dimensional relationship between the bcc and sapphire lattices. This relationship is sketched in fig. 5(a). Moreover in a fourth case in which bcc (100) is grown epitaxially on Al₂O₃ (1102), the observed tilt ~3° of the resulting epilayer agrees closely with that arising from the 3D relationship (McWhan 1985). It has further been discovered that a number of other bcc metals including Mo and V



Fig. 5. (a) Orientations of Nb and other bcc transition metal overlayers on sapphire $(2\overline{1}\overline{1}0)$, $(0\overline{1}10)$ and (0001) surfaces conform to the 3D relationship shown, where the Nb cube has its [111] body diagonal perpendicular to the sapphire basal plane. Note how the sapphire $(0\overline{1}12)$ and Nb(001) have similar orientations. (b) Six orientations, in which hcp Ti can be grown by MBE on bcc buffer layers prepared on sapphire substrates, are indicated by the bold lines.

conform to the same pattern (Flynn and Yadavalli 1992) although discrepant tilts of the (100) orientation are frequently observed. The origins of these most interesting epitaxial effects have since been traced for Nb/Al₂O₃ interfaces by Ruhle's Stuttgart group (Mayer et al. 1992) using high resolution electron microscopy. The fixed 3D relationship has its origins, as expected, at the atomic level in the bonding of the metal atom into the oxide lattice (Mayer et al. 1992). Extraordinarily narrow component mosaic spreads have been observed (Reimer et al. 1992) under some circumstances, and mainly for the (110) Nb orientation. It is believed that in these cases the Nb planes are unusually well aligned with the Al₂O₃ planes, perhaps with strain relief assisted by mobile H impurities (Reimer et al. 1993) and that this allows the metal to mimic the narrow mosaic spread of the oxide itself. Fine structure related to interfacial registry has been observed on the sharp line (Elliott 1972).

The first synthesis of (0001) rare-earth superlattices by Kwo et al. (1985b) took place on bcc templates provided for this purpose, specifically of Nb (110), rather than Ir (111) used earlier for Ru (0001) (Cunningham and Flynn 1985). The observed growth of Y on its basal plane conforms to the Nishijima–Wasserman relationship in which the nearest neighbor spacings for the two lattices lie parallel. Excellent growth of other rare earths takes place on Y near 400°C with limited interdiffusion. While the X-ray peaks have widths comparable to Nb along (0001), a generally larger mosaic spread of perhaps a quarter of a degree is observed, for reasons that remain to be identified. Indeed, large annealed crystals of rare earths are observed by X-ray methods (Gibbs et al. 1986, 1988, Isaacs et al. 1989) to be a good deal more perfect than any epitaxial materials produced to date. It will be of interest to employ extraordinarily aligned Nb (110) (see above) as the template for rare-earth growth.

3.2. Other orientations of hcp lattices on sapphire

Some indication of future opportunities for rare-earth growth may be obtained from consideration of progress for alternative hcp metals. We illustrate this point with reference to the case of hcp Ti. Titanium has been grown by Huang, Du and Flynn (Huang et al. 1991a) as an epitaxial crystal of high quality in six alternative orientations. These include the basal plane (0001), the prism plane (1120), and a sheaf of orientations based on (110n) with n = 0, 1, 2, 3. All of them are depicted in fig. 5b. In all six cases the synthesis proceeds from Al₂O₃ through a refractory bcc metal, and while much remains to be learned about the several nucleation processes involved, the pathways involved seem reproducible and stable.

Parallel investigations of rare-earth growth are lacking at present, and there is no reason to think that precisely analogous results will be forthcoming. It is nevertheless apparent that important new research will be facilitated by the availability of epitaxial rare earths in a variety of orientations. Also, by comparison with the controlled diversity of results for Ti, it would appear surprising if at least some rare-earth orientations, in addition to the basal plane, were not accessible by similar methods. In addition the crystal grower has available certain alternative techniques such as grading. Thus (Massalski 1986) Zr forms a complete range of solid solutions with Ti, and Sc, which fits well on the Zr lattice, is continuously soluble with Y. Thus avenues appear open for the synthesis of Y/rare-earth systems from Ti in any of the known Ti orientations.

3.3. Other substrates

Rare earths have been grown successfully starting from three other alternative substrate crystals. First among these is homoepitaxy of Y using large single crystals, followed by rare earth growth on Y. A procedure has been refined by Du, Tsui and Flynn (Du et al. 1988) for the sputter-cleaning and subsequent homoepitaxial regrowth of a- and b-axis bulk Y. Hexagonal materials tend to grow best on their basal planes. Indeed, some curious phenomena are observed by RHEED in a- and b-axis growth of rare-earth metals. Specifically, the a and b surfaces reconstruct in a hexagonal pattern resembling the basal plane. X-ray analysis of the grown crystal nevertheless reveals high quality material of the selected orientation. Thus material laid down on the hexagonal reconstruction must progressively transform into the correct orientation as it becomes buried by successive new layers. Presumably these aspects of the growth behavior are common to lanthanide materials derived from all starting substrates, not just bulk crystal, although this supposition lacks confirmation at present.

A second starting point for rare-earth growth (Du et al. 1988) is the preparation of thin freestanding Nb crystals from foil 10μ m thick by means of an annealing procedure. Both (110) and (111) foils prepared in this way lead to good single crystal material, although the slightly wrinkled character of the foil is reflected in a wide apparent mosaic spread of the resulting rare-earth samples.



Fig. 6. Temperature dependence of the magnetization in one half of a monolayer of Gd at various fields applied perpendicular to the c axis.

Artificial fluoride mica, properly named fluorophlogopite, provides an interesting and important new substrate (Tsui et al. 1993b) for rare-earth growth. Its advantage over natural micas such as ruby muscovite is that it exfoliates only above 1200 K. This permits the growth of refractory bcc buffers and thence rare earths. The second advantage of mica is that it can be cleaved down to a thickness comparable with epitaxial films. This provides an important means to eliminate of substrate-derived signals, as in thin-film magnetic or optical measurements. It has been possible, for example, to measure the magnetism of lanthanide coverages down to 0.1ML by these means. Figure 6 shows as an example the temperature dependence of magnetization for $\frac{1}{2}$ ML of Gd at various fields, according to Tsui, Han and Flynn (1993b). Mica also has several disadvantages. In the first place its template is weak and essentially hexagonal. Second, bcc metals grow upon it in their (110) orientation, and so form a threefold domain structure of these tetragonal surfaces. Fortunately the rare-earth (0001) planes grow on these domains, and knit together after 300 Å to form a reasonably good single crystal that gives satisfactory RHEED streaks. In this way artificial mica offers a potential solution for numerous sensitivity problems in thin-film measurements. As will be made evident in sect. 4, the magnetic data exhibit detailed changes on the 1ML scale of coverage that themselves confirm that the tailored structures are sharp and flat. At the time of writing microscopy evidence is coming available (Zhou 1995) that points to the presence of pinholes in the films, so caution may be needed until the nucleation problems signalled by these pinholes are brought under control.

3.4. Tilted films

A further capability that again remains to be placed in service for rare-earth research is the growth of vicinal crystals that are tilted away from low index planes. One means by which this can be achieved is to grow on miscut substrates such that the optical surface lies at a selected angle with respect to the crystal planes. For example, miscut ($11\overline{2}0$) sapphire successively gives tilted Nb (110) and tilted Y (0001). It is generally observed that the Bragg scans along the crystallographic normals ($11\overline{2}0$), ($11\overline{0}0$) and (0002) in the three cases, lie close to the same line through reciprocal space, which shows that the successive crystal planes are almost parallel. This affords a general procedure for the growth of vicinal rare earths from vicinal epitaxial grade sapphire.

A second way to produce controlled tilt has been demonstrated for rare earths but as yet only for the $(1\bar{1}02)$ growth plane (Du and Flynn 1990; for a review see Flynn 1991). The "magic" (211) planes of bcc metals, when grown on Al₂O₃ (1 $\bar{1}00$), undergo disordering by displacement of atomic rows. Unusually long and smooth RHEED streaks from the remaining scattering planes are associated with this 1D order. On these surfaces the rareearth metals grow with a 1D pseudomorphic strain for several monolayers (Huang et al. 1991b). Du and Flynn (1990) find that at thicknesses of tens of monolayers the rareearth crystals undergo a spontaneous tilt through an angle that relieves the strain while retaining atomic registry at the interface (Du and Flynn 1991). Tilt angles in the range 0–7° achieved by these methods can be predicted and designed to 0.1° precision simply from the lattice parameters employed. The symmetry breaking required to drive tilt in only one sense, and hence produce a tilted epitaxial single crystal, is achieved by the use of sapphire with a small vicinal miscut.

4. Magnetism of epitaxial rare-earth crystals

The properties of rare-earth metals are, in general, modified when these metals are grown epitaxially. Here our interest centers specifically on magnetic properties. Changes in the magnetic properties of thin, epitaxial crystals arise from two main causes. First is the physical effect of epitaxy in straining an epilayer to lattice spacings that differ from those of the bulk crystal. This encompasses the stretching or compression of the growth plane, together with any accompanying changes of the perpendicular strain required by mechanical equilibrium, in order to satisfy the requirement that the film remain in registry with its substrate. In thicker films, these strains may, in part or whole, be relieved either by interfacial slip or by plastic processes in which dislocations cause the average lattice spacings to be position-dependent. The second main perturbation of bulk behavior is the effect of geometry on electronic properties. This second topic includes geometrical effects, in which behavior is modified, for example by the dimensionality of the tailored system, and chemical effects in which the interfaces between the epilayer and substrate materials cause the properties to change. It is helpful to identify three broad regimes of behavior defined by these effects. We refer to them as the thick-film limit, the epitaxial crystal regime, and the interfacial limit. In the first of these regimes the behavior is dominated by plastic relief of the epitaxial strain, and the properties tend to those of the bulk material as the thickness is increased. In the third, the properties are dominated by interfacial geometry and chemistry. We can readily fix the order of magnitude of the film thicknesses relevant to each regime. Plastic relief in metal films with 1% misfit typically becomes important for film thicknesses greater than 100 Å when grown at ~3/8 $T_{\rm m}$; unrelaxed films an order of magnitude thicker may be grown at lower temperatures at some cost in crystal quality. Interfacial effects dominate for films no more than a few atomic layers thick because metallic screening takes place on the length scale of a fraction of an atomic spacing. These constraints leave the typical thickness range $10\text{\AA} \leq d \leq 100\text{\AA}$ in which a good epitaxial film is more or less uniformly strained and yet only modestly perturbed by interfacial chemistry. We describe the available results in this regime first in what follows.

4.1. Epitaxial crystal regime

In this regime, the epitaxial film behaves as a perfect crystal that is elastically strained. Properties in this regime should thus, by definition, be predictable from the properties of bulk single crystals in the presence of uniform elastic strains. Unfortunately, data on the common thermal and mechanical properties of thin films are lacking for this range of thickness, owing mainly to the difficulty of such measurements. Transport properties are easier to measure but may be dominated by geometrical and interfacial effects.

Magnetic phenomena can be probed with monolayer sensitivity; a good general review is given by Falicov et al. (1990). For the particular case of the lanthanides, of interest here, the magnetic properties offer the attraction of a rich phase structure outlined in sect. 2. These magnetic phenomena would remain largely unchanged in the epitaxial regime were they not coupled to mechanical behavior through the strong magnetostriction described above in sect. 2.3. There are two main effects of epitaxy. First, *epitaxial strains* of several percent, typical of epitaxial misfit in metals, are sufficient to cause profound changes of magnetic properties. The second main effect of epitaxy is the *clamping* of the epitaxial strain at a fixed value which is defined by the frozen epitaxial registry on the substrate. Clamping tends to prevent an epitaxial crystal from undergoing the same magnetostrictive changes as the bulk during phase transitions, which again profoundly modifies the epitaxial phase diagram. Some experimental observations are discussed on the basis of these ideas in what follows.

4.1.1. Gadolinium

Thin films of Gd have been grown on Y (Kwo et al. 1985a,b, Kwo 1987), Dy (Camley et al. 1990), and synthetic mica (Camley et al. 1990). None have been studied carefully as a function of film thickness and strain. However, as magnetostriction is weak in Gd, even at the Curie point, the perturbation caused by pseudomorphic strain should be small. In agreement with this expectation the Gd Curie temperature is never observed to differ from

its bulk value of 293 K by more than a few degrees. Detailed comments on geometrical effects in thin Gd systems are deferred to part 4.3 of this section.

4.1.2. Dysprosium

The most complete studies of the epitaxial regime to date have been made on Dy epilayers (Kwo et al. 1988, Farrow et al. 1991). The interest of this case derives from its strong and elaborate magnetostrictive behavior. This includes the large orthorhombic distortion (see sect. 2) associated with two phase transitions. One is the first order Curie point at about 85 K in the bulk, which is accompanied by strong magnetostriction, and the other is the second order paramagnetic-to-helical transition at the Néel temperature, at about 178 K in the bulk, which causes only weak magnetostriction. A comparison between the two transitions is thus of considerable relevance.



Fig. 7. Magnetic phase diagram for epitaxial Dy thin films grown on (0001)Y-Lu alloys. The phase boundary intercepts the $H_c = 0$ plane along the line of strain-dependent Curie temperatures $T_c(\varepsilon)$.

The investigations (Tsui and Flynn 1993) employed $Y_x Lu_{1-x}$ alloys to vary the pseudomorphic strains of 50 Å Dy layers from +1.6% for x=1 to -2.6% for x=0. These layers are thin enough for the films to be largely unrelaxed, as required for epitaxial crystals. Measurements of magnetization M and critical field H_c were used to probe the magnetic state as a function of temperature. The results obtained using alloy templates are represented by open circles in fig. 7. They are consistent with striking earlier (Beach et al. 1993b) studies of Dy epilayers on pure Y and on pure Lu, indicated in fig. 7 by solid circles.

One of the first discoveries of the earlier research (Salamon et al. 1986) was that the Y template completely suppresses the equilibrium ferromagnetic phase. LaF₃ (Farrow et al. 1991) and later Lu and Zr (Luche et al. 1993) were found to enhance the T_C of Dy films respectively to $\geq 86 \text{ K}$, $\geq 160 \text{ K}$ and $\geq 150 \text{ K}$ from 85 K. The relative strains of +1.6% and -2.6% associated with perfect pseudomorphism on Y and Lu, and the absence

of such strain on LaF₃, permit a clear identification of the Curie point suppression and enhancements as consequences of the epitaxial expansion and compressions. It was found that a metastable magnetized phase of Dy on Y could be induced by a 2.6 kOe field at low temperature only on films thicker than 76 Å (Kwo et al. 1988).

A second important discovery (Beach et al. 1993b) was made using synchrotron radiation to study the epitaxy of Dy on Lu. The driving force for Dy magnetostriction turns out to remain sufficiently strong that it distorts both the Dy and the surrounding Lu in the thin film. The main results were obtained by in-plane X-ray scans on superlattices rather than epilayers, and are described in sect. 5 below. However, the magnetic behavior in the films was so similar to that in superlattices that it permits the inference that the same phenomena occur in the films. At temperatures below $T_{\rm C}$ the X-ray results show that the entire basal plane distorts into in-plane orthorhombic domains oriented along the three easy *a* directions. The distortion is not present above $T_{\rm C}$. It can therefore be associated unambiguously with the magnetization process.

Results for pseudomorphic films on Y, Lu and their alloys, together with films partly relaxed on the pure templates, provide the "c-axis epitaxial phase diagram" for Dy magnetism shown in fig. 7. There, the critical-field surface is seen as a function of temperature and basal plane strain ε . Clearly, the onset of helimagnetism at 178 K is relatively insensitive to ε . In contrast the ferromagnetic transition, which by definition takes place where $H_c(T) = 0$, incurs a large magnetostriction and is seen to be strongly dependent on ε . The phase diagram in fig. 7 connects the helimagnetic phase at $\varepsilon = 1.6\%$ (Dy on Y) for which H_c remains nonzero as $T \rightarrow 0$, through to the enhanced $T_C \approx 160$ K at $\varepsilon = -2.6\%$ (Dy on Lu). T_C rises rapidly from zero at ε slightly positive, and approaches T_N as ε nears its value for the Lu template.

Results of the type shown in fig. 7 make it possible for the first time to separate the effects of strain and clamping on the magnetic properties of the epitaxial crystal. The entire diagram displays the dependence on the two principal state variables T and ε . The consequence of clamping alone may be seen by comparing the critical field of bulk (unclamped) Dy with that of the epitaxial film with the same lattice spacing, namely at $\varepsilon \approx 0$. The bulk behavior, shown by the thick line in fig. 7, lies surprisingly close to the epitaxial results. This establishes that the effect of clamping on Dy magnetism is relatively small. The result is unexpected because the elastic energy must have the same order of magnitude as the exchange and magnetic energy changes at the transition, and its clamping might reasonably cause larger changes of state.

A tentative explanation advanced for this result (Tsui and Flynn 1993) is that the thin magnetic crystal breaks into magnetic domains having in-plane dimensions comparable to the film thickness. The domains possess orthorhombic in-plane distortions along the axes of easy magnetization, similar to the structure observed in Dy/Lu superlattices (see sect. 5.2.1.5) such that the mean in-plane strain vanishes. Domains that have the smallest possible lateral extent then incur the least strain energy of the surrounding Lu lattice. Modeling of this type can be made quantitative by noting that the elastic strain field must extend the Dy strain ε into the surrounding Lu over a distance comparable with the domain size *l*. The strain energy per unit area is then $E_s = cl\varepsilon^2$, with *c* an elastic constant. Figure 8a



Fig. 8. (a) Schematic diagram of a magnetic domain in an epitaxial film. (b) Nonuniform elastic strain fields extend over a region of dimension l that is larger than the magnetic-film thickness d. The resulting energy of the film vs strain is sketched here.

is a sketch showing a domain in the thin film. The magnetoelastic coupling is linear in strain, much as in the Jahn-Teller effect. This provides a leading ε -dependent term $-\alpha\varepsilon l^2 d$ per domain, proportional to the domain volume $\sim dl^2$. The magnetoelastic energy per unit area is thus $E_{\rm me} = -\alpha\varepsilon d$, with α a coupling constant. The energy is minimized for the strain ε_0 and energy $W_{\rm min} = E_{\rm me} + E_{\rm s}$, given by

$$\varepsilon_0 = \frac{\alpha d}{2cl}; \qquad W_{\min} = -\frac{\alpha^2 d^2}{4cl}.$$
 (11)

as sketched in fig. 8b. Finally, the addition of a domain boundary energy per unit area of film given by $E_d = bd/l$, with b proportional to the energy per unit area of boundary, makes the total energy of the distorted phase

$$W_{\rm t} = \left[b - \frac{\alpha^2 d}{4c}\right] \frac{d}{l} \tag{12}$$

relative to the undistorted phase.

For sufficiently thick films the second term in the bracket always prevails; W_t is then negative and the total energy is least for the minimum l. The modeling breaks down when $l \approx d$. It is nevertheless clear that no energetic gain can accrue from making the domains much smaller than d, because the neighboring nonmagnetic lattice no longer distorts. Hence the final prediction of a minimum energy when $l \approx d$ does appear realistic within this framework. When, on the other hand, b exceeds the second term in the brackets, then W_t is positive, and the energy is then least when the distortion is zero and the domain size infinite. This means that the ferromagnetic phase of lowest energy no longer exhibits magnetostriction. Whether or not this newly predicted phase is ever preferred over the helimagnetic phase and can occur in practice remains to be determined from the exchange energy $\mathcal{J}(q)$.

The simplified analysis outlined above pertains directly to the epitaxial phase diagram of Dy in fig. 7. It suggests that the effect of clamping is *not* in fact negligible,

despite the apparently weak perturbation of H_c associated with epitaxy, but is associated instead with magnetic microstructure. Specifically, the epitaxial phase diagram is almost unchanged near $\varepsilon = 0$ because the 50 Å crystal breaks into magnetostrictive domains that minimize the clamping perturbation of the surrounding Lu lattice. The explanation is consistent with the observations but at the time of writing lacks independent verification.

The behavior of still thinner epitaxial Dy crystals on nonmagnetic templates near $\varepsilon = 0$ remains of considerable interest, in view of the crossover of the two terms in W_t with decreasing thickness d, apparent in eq. (12). For the present there are no experimental results that probe these phenomena in sufficient detail. Further reference to this matter is made in sect. 4.3.

4.1.3. Erbium

Considerable interest is attached to the magnetism of erbium layers. Even when grown on its basal plane, this lanthanide exhibits strong magnetic anisotropy that prefers perpendicular spin polarization along c rather than the in-plane polarization favored by the demagnetizing field. As noted in sect. 2.3, magnetostriction causes a 0.32% expansion along c and a 0.16% contraction of the a-axis at the ferromagnetic transition of the bulk crystal. The transition takes place when the energy gain achieved at $T_{\rm C}$ in the ferromagnetic phase from magnetoelastic terms in the free energy (1.01 J/cm³), equals the exchange energy difference between the ferromagnetic and CAM phases. Thus, the effects of epitaxy-induced strain in epitaxial Er are expected to be significant.

There is an important difference between Dy and Er in the way magnetic domains can avoid the clamping constraint. The preferred perpendicular magnetization of caxis Er epilayers can accommodate only two distinguishable domain types, namely up and down polarizations. By symmetry these must give identical magnetostrictions. Therefore Er is not able to avoid the epitaxial clamping constraint by domain formation in the way described above for Dy. These arguments lead to the expectation that both strain and clamping may produce strong changes of the Er epitaxial phase diagram. Careful investigations of the epitaxial phase diagram have not been completed at the present time. However, in agreement with the general expectations, it is observed that the ferromagnetic phase of Er thin films is suppressed both when stretched on Y (Borchers et al. 1988a) and when compressed on Lu (Beach et al. 1991). The magnitude of the effect is made clear by the observed critical fields for ferromagnetism which decrease to zero (i.e. spontaneous magnetism) only for film thicknesses exceeding about 1µm on Y (Borchers et al. 1991). This shows that substrate effects are indeed much less easily relieved for Er than for Dy, as anticipated for the domain effects outlined above.

Calculations of magnetic behavior have been performed using the assumption that the elastic and magnetoelastic coupling constants in an epitaxial Er film are identical with those of bulk Er (Borchers et al. 1991). The calculation is able to explain the suppression of the ferromagnetic transition and to predict the critical magnetic field required to recover

the ferromagnetic state. In the limit of a thick Y layer, the Er film is clamped at a strain ε_0 , and this reduces the magnetoelastic energy gain to

$$\Delta E_{\rm me} = \hat{c}\varepsilon_0^2 - \widehat{K}\varepsilon_0 - \frac{K_z^2}{2c_{33}},\tag{13}$$

where

$$\hat{c} = c_{11} + c_{12} - \frac{2c_{13}^2}{c_{33}}, \qquad \hat{K} = K_x + K_y - \frac{2c_{13}K_z}{c_{33}}.$$
 (14)

The c_{ij} and K_j are the elastic and magnetoelastic constants, respectively (see sect. 2). The coefficient \hat{K} is negative for Er, and this causes the magnetoelastic energy to become less negative for positive ε_0 , which is the case for Er grown (0001) on Y. It is demonstrated in sect. 5 that this simple formulation accurately predicts the critical fields for both superlattices and films. The success of the calculation for Er relies on the assumption that the epitaxial constraint cannot be avoided by domain formation, which is consistent with the *c*-axis magnetization of Er grown on its basal plane, and provides an interesting contrast with the behavior of Dy, as discussed above.

Systematic studies of the effect of epitaxy on spin slips and their lock-in states are in their initial stages. Studies of Er on Y and Lu (Tanaka et al. 1995, Beach et al. 1991) reveal strong changes of the bulk lock-in strengths, which differ markedly in the case of stretched basal plane (Y) and compression (Lu). In the former case, several strong lock-ins persist over extended temperature ranges, while the lock-ins of Er on the Lu substrate are notably weakened. At the time of writing, these interesting changes remain still to be interpreted.

4.1.4. Other systems

While a number of other lanthanide systems have been prepared as multilayers, few have been examined systematically as epitaxial films. The Oxford group, Jehan et al. (1993), report that 5000 Å of Ho on Y exhibits clearer spin-slip structures than the bulk. They also report that T_N is depressed by ~1 K, and the low-temperature $c^*/6$ phase is absent.

Alloys offer important new insights into the effects of epitaxy. Results are available (Everitt et al. 1995) for the magnetic behavior of thick Dy-Lu alloy films grown epitaxially on Y (0001). When plotted against the de Gennes factor, the Néel temperatures of these films are completely consistent with other alloys. Preliminary magnetic X-ray scattering studies indicate the presence of lock-in (or spin-slip) structures in the alloys, even though no such phases are evident in pure Dy films. Epitaxial Nd films have also been grown on Y and as superlattices, but this work is still in its preliminary stages.

4.2. The thick-film limit

The properties of epitaxial systems must systematically approach those of the bulk material as the thickness of the epitaxial layer is increased. The way this happens depends on the particular property. With increasing film thickness the interfacial electronic and vibrational behavior is simply overwhelmed by the volume dependence of the bulk; these effects are one topic of sect. 4.3. On the other hand, the lattice parameter is strongly influenced by elasticity constraints. It is a fact that the equations of elastic equilibrium contain only uniform solutions (i.e. constant strain, independent of the position x, y, z) when planar symmetry is required. This must be the case for idealized epitaxial films. Given a particular atomic registry at the interface, the only elasticity constraints make all epitaxial system, regardless of its thickness, is the state of uniform strain that is consistent with the given registry. In short, elasticity constraints make all epitaxial systems into epitaxial crystals (in the sense defined above), however thick they may be. Superlattices are subject to the same restrictions, provided that the interfaces are transitive.

An understanding of strain effects in films is of critical importance for our subsequent discussion of superlattices in sect. 5. The topic of strain relief through interfacial accommodation began with Van der Merwe's treatment of critical thickness for the formation of interfacial dislocations (Van der Merwe 1950, 1962) and has been the subject of reviews (Matthews 1979, Freund 1993). In the interest of brevity we present only a sketch of strain relief phenomena in what follows, and illustrate the substance of the discussion by relevant examples of magnetic behavior in thin rare-earth films.

4.2.1. Strain relaxation

The fact that real epitaxial layers of sufficient thickness tend towards bulk behavior demonstrates that the elastic constraint described above is, in practice, relieved. Anelastic processes therefore take place in the growing film, or in any event prior to examination, for example during cooling. That this must necessarily happen is apparent upon energetic grounds. Suppose that an epitaxial strain ε originates at the interface between the crystal and its template. The elastic strain energy per unit area is then $c_{ii}\epsilon^2 d/2$, for a film of thickness d, in which c_{ij} is the appropriate elastic constant. Suppose also that the strain ε occurs at an interface for which the strain ε_0 would correspond to perfect registry, so that $\varepsilon - \varepsilon_0$ represents interfacial relaxation. Then the interfacial misfit creates $(\varepsilon - \varepsilon_0)/|b|$ interfacial dislocations per unit length, with b the Burgers vector. This introduces an interfacial energy per unit area of $2w|\varepsilon - \varepsilon_0|/|b|$, with w the line energy per unit length of dislocation. By minimizing the sum of the two energies with respect to the strain one finds that the epilayer exists at a uniform equilibrium strain $\varepsilon = \varepsilon_0$ when $d < d_c = 2w/|b|c_{ij}\varepsilon_0$, and at the smaller value $\varepsilon = 2w/|b|c_{ij}d$ for $d > d_c$. The critical thickness d_c , in this simple approach provides the upper bound on the fully pseudomorphic epitaxial crystal of sect. 4.1. Thicker epilayers still remain uniform epitaxial crystals in this approximation, but are less strained.

During the growth of real crystals the strain relief must take place continuously, and some of the anelastic strain most probably remains in the epilayer rather than in the interface. Furthermore, the final state of strain is observed to depend on the growth temperature (Dodson and Tsao 1987, Tsui and Flynn 1995, Tsui 1992) which indicates
that an activated component is present in the kinetics. While the mechanisms of plastic relief themselves are of considerable interest and technical importance, the specific inhomogeneous configurations that are created in this way have no special significance. Nor are the detailed processes well understood.

This brief background in strain relief can serve to illuminate the resulting effects on thin-film magnetism. The following point is of particular importance. Suppose that the crystal does, as suggested above, achieve and maintain a specific state of uniform strain ε as a result of the growth procedure. Then, to a good approximation, the temperature dependence of its magnetism must just be the section of the epitaxial phase diagram that corresponds to the particular orientation and strain. Indeed the epitaxial phase diagram is obtained precisely from measurements of this type, but for thin, unrelaxed epilayers. A critical question is whether or not thicker, partly relaxed epilayers exhibit identical behavior for the same actual strain ε . If this is the case it indicates that the interfacial registry that defines the partly relaxed misfit strain ε is independent of any applied magnetic field. Otherwise the field dependence of the misfit would cause the state to pass along a different path across the surface of state as the temperature changes. This discussion has neglected differences of expansion coefficients and anelastic evolution subsequent to growth, but these types of elaborations can be incorporated as needed. The distinction identified here is important in connection with the possibility that mechanical damage accompanies magnetic cycling. There is a further connection with the metastable magnetized state that can be induced in Dy films more than 76 Å thick grown on Y substrates.

4.2.2. Effect on the phase diagram

Available results indicate that partial relaxation in fairly thin films does leave them in reasonably uniform states of strain, and therefore must largely be interfacial. The solid points in fig. 7, other than those for films unrelaxed on Lu and Y, actually were taken from partially relaxed thin films (cf. fig. 4). The fact that they conform accurately to the surface defined by unrelaxed systems indicated that their state of strain remains frozen at the part-relaxed value specified by the location of the points along the ε -axis. Thus, they approximate epitaxial crystals but with modified interfacial registry.

Most revealing among available data for a wider range of behavior are the critical fields of *b*-axis Dy grown epitaxially on Y (100) with various thicknesses (Tsui 1992). Figure 9 shows how the critical field depends on temperature and film thickness for Dy grown along the *b*-axis. An approximate continuous surface is drawn through the scatter of the data points. It indicates that the first 50 Å has a special temperature-insensitive behavior with a critical field near 10 kOe that is relatively large. Films over 100 Å thick have critical fields that vary with temperature very much like sections of the *c*-axis epitaxial surface (fig. 7), with ε positive. The results for the thinnest films suggest that relief of the pseudomorphic strain sets in at about 50 Å. An alternative explanation that interfacial effects cause strong changes of magnetic state below 50 Å can be discounted on the basis of other results described in sect. 4.3. For the thicker *b*-axis films note that the *a*-*c* growth



Fig. 9. Magnetic phase diagram for *b*-axis Dy/Y superlattices and *b*-axis films up to $1 \mu m$ thick. The lower surface (solid lines) separates the helimagnetic and fan phases, the upper surface (dashed lines) marks the saturation fields. The bulk limits are shown in the foreground.

plane is anisotropic and thus quite different from the isotropic in-plane strains of the c-axis case. The existence of close similarities between c-axis and part-relieved b-axis magnetic properties is in this respect remarkable. A straightforward explanation of the data would be available if the b-axis films thicker than 50 Å were relaxed to a strained configuration sufficiently similar to that of the partly relaxed basal plane case that the magnetic behaviors also became similar. Detailed exploration of these possibilities has been hindered by the difficulty of determining the precise strain states of thin epilayers on thick templates.

Similar but less complete results are available for Er films (Tsui 1992). The Néel temperature changes at most by $\sim 1 \text{ K}$ as the film thickness is reduced to 400 Å. Results showing the change of the ferromagnetic transition for Er on Y are presented in fig. 10a. There, the critical fields as functions of temperature for two Er crystals 1750 Å and 9500 Å thick are compared with the bulk behavior. Neutron scattering data for the 3950 Å film is shown in fig. 4. Evidently ferromagnetism is never recovered in these films for temperatures above 10 K, although the precise behavior



Fig. 10. (a) Critical field vs temperature for bulk Er, 1750 Å and 9500 Å films; (b) dependence of the critical field at 10 K (solid points) and 20 K (open circles) on film thickness.

for films 1μ m thick may be sensitive to details of the growth procedure. Figure 10b shows the available results for *c*-axis films. Both Dy and Er exhibit a complete suppression of ferromagnetism in the thinnest films, as detailed above. However, they differ considerably in the film thickness required to restore bulk properties, as noted in the discussion of domain effects above. As fig. 10 makes clear, a 3 kOe field is required to restore ferromagnetism at 10K in an Er film as thick as 1 μ m, while

a comparable field induces ferromagnetism in a Dy film only 20 nm thick at 30 K (Kwo et al. 1988).

4.2.3. Effects on the magnetic state

Thus far we have used the shift of phase equilibrium to monitor the influence of epitaxial strain on the competing magnetic phases. Each phase undergoes changes of energy and structure caused by the existing strain. These alter the balance of the free energies and thereby shift the phase boundaries. The quantities of direct physical interest are of course the individual free energy shifts themselves, and the structural changes of the phase from which they arise. In certain cases it is possible to probe structural changes directly, in order to obtain a direct relationship between epitaxy and structure. This is most readily possible for the helimagnetic phases, for which neutron scattering provides a direct probe of both the wavelength and amplitude as a function of temperature. Selected results for Dy and Er are discussed in what follows to clarify the present understanding of the strain-induced changes.

In the helimagnetic phase of bulk Dy the turn angle per layer is about 43° near the Néel temperature of 178 K. With decreasing temperature it decreases smoothly to about 26° at the Curie point, where it falls immediately to zero in the ferromagnetic phase. Epitaxy tends to increase the turn angle and to suppress its fall to zero. Even a 200 Å Dy film remains in the helimagnetic phase at 80 K (5 K below the bulk transition), with a turn angle of 27°. In a more extensive study of Er films (Borchers et al. 1988a, 1991) the phase angle in films as thick as 9600 Å are always larger at a given temperature than in bulk Er. Added evidence of the influence of epitaxial strain is that 600 Å of Er grown on *c*-axis Lu, which gives a basal plane compression, has turn angles systematically smaller than the bulk at each temperature (Beach et al. 1991). Magnetic X-ray scattering confirms these results and shows that Y enhances certain Er lock-in states while Lu suppresses them (see below) (Tanaka et al. 1995).

Efforts have been made to reproduce the observed trends of structure modification by epitaxy using models for the several terms in the free energy of the helimagnetic phase. The main contributions are the exchange energy, the magnetoelastic energy and the Zeeman energy. Of these, the last two can be represented reasonably well by means of measured moments and magnetoelastic data. Unfortunately, the exchange energy is not well known. It is often simulated by the simplest theoretical model that predicts helimagnetic behavior, which employs three exchange constants: J_0 , coupling nearest neighbors within a plane, J_1 , nearest-neighbors on adjacent planes, and J_2 , next-nearest neighbor planes (Cooper 1972). When bulk turn angles are used to fit the model, the exchange constants for the first and second planes turn out to be strongly temperature dependent (Tsui 1992). Further, even within this 3-J model, the turn angles vary from plane to plane due to end effects in thin-film structures (Jensen and Mackintosh 1991, Bohr et al. 1989). In reality the couplings predicted by the RKKY interaction have a long range, and with the awkward feature of near-cancellation among many terms with opposing signs. A useful basis on which to build an analysis of the thin-film effects remains as yet to be formulated.

Neutron scattering measurements such as shown in fig. 4, reveal similar modifications of wave vector in the CAM phase of Er. As Q(T) changes with temperature in bulk Er, as described in sect. 2.2, its magnitude passes through values that are commensurate with the lattice periodicity itself, and lock-in occurs at various commensurate structures. These are shown as a solid line in fig. 11. Each commensurate structure corresponds to a specific magnetic wave in the lattice. These are longitudinally polarized at higher temperatures, develop a helimagnetic component at intermediate temperatures, and have a cone structure at low temperatures. The behavior of Q(T) in thin films and superlattices gains added interest from the opportunity to examine the way epitaxy modifies these well defined magnetic structures and changes their coupling to the lattice. Lock-in states of a similar character can occur for spiral antiferromagnets such as Dy and Ho. They are, however, weak for Dy because its small in-plane anisotropy blurs spin-slip structure, and the stronger lock-in behavior of bulk Ho has not yet been traced into epitaxial films. The present illustrative examples are therefore confined to the case of Er.

Results for the turn angle of two Er (0001) films on Y grown, respectively 860 Å and 9500 Å thick are described here. The strongly perturbed periodicities of (i) the (0002) satellites from the c-axis modulation (CAM: open circles) and (ii) the superposed basal plane spiral (solid circles) at low temperature, are shown for the 860 Å crystal in fig. 11a. For comparison the bulk behavior is indicated by the solid line. It is apparent that the wavelength of the CAM is clamped in a narrower range of large q values by the epitaxial constraint. A point of considerable interest is that the specific bulk spin configurations marked 2/7 [4 up-spins and 3 down-spins per magnetic unit cell] and 4/15 [41413141] for the bulk are greatly enhanced in the epitaxial film, although others appear to be suppressed. In the c-axis field-dependent magnetizations, shown in fig. 11b, these two states (which have net magnetic moments) are marked B1 and B2, coinciding with sharp features. In thicker epitaxial films the periodicities are less perturbed from bulk values, and the wavelengths of the CAM and basal plane spiral appear more nearly equal. This is illustrated by the example of a 9500 Å Er epilayer on Y in fig. 11c. The resulting magnetic signature shown in fig. 11d consists of sharp features under conditions that correspond to the 2/7 and 6/23 lock-in states.

Recent results by Tanaka et al. (1995) confirm the observations for Y substrates and reveal interesting differences caused by basal plane compression on Lu substrates. The lock-in states are much weaker and the turn angles are uniformly smaller. Lock-in to $Q=0.25 c^*$ takes place just below 30 K.

Without question the results summarized here afford just a first glimpse of a rich field in which the magnetism of epitaxial films responds in an interesting and sensitive manner to the epitaxial constraint. The actual state of strain in this limit depends on both the film thickness and the growth conditions. In turn the magnetic state must depend on the state of strain and other factors that may influence, for example, the magnetic domain structure, in addition to the natural variables of field and temperature. An eventual complete description must include the statistical behavior of the spin-slip system.





4.3. The thin-film limit

As the thickness of a film is reduced, the pseudomorphism is improved and the state of strain generally becomes more uniform. At the same time, however, the definition of magnetic phase structure may be complicated by boundary effects, and the sharp symmetry distinctions among alternative phases is blurred. For a recent review of thinfilm magnetism see the article by Falicov et al. (1990), which deals mainly with transition



Fig. 11cd. Same as fig. 11a,b, for a 9500 Å film.

metals. The theory of phase transitions and dimensionality is reviewed by Stanley (1971). Here we are concerned instead with particular effects that are important for rare-earth thin films.

As a specific example to clarify the effect of reduced film thickness consider the helimagnetic phase of Dy, which has a *c*-axis wavelength of about 30 Å. The structure has a net moment, and is no longer clearly an antiferromagnet, when the film thickness

falls below 30 Å. It is reasonable to anticipate, in addition, that the end effects at the two surfaces of the film change the turn angle and make it vary with depth. Still worse, the distinction between a helical phase and a ferromagnet is almost entirely lost as the film thickness is further reduced to about two layers in a typical lanthanide with a magnetic period of 10 atomic layers. Finally, the reduced dimensionality has two profound effects on magnetism by first confining the magnetic interactions to spins located in a thin slice of material, and second by ensuring that all moments exist in an environment of perturbed crystal field. In addition it is likely that continuity in monolayer films is broken by the terrace structure of the original substrate template. These various independent phenomena combine to determine the magnetic behavior in what we term the thin-film limit. The behavior of films has obvious consequences for superlattices which comprise films coupled through spacer layers. A further fundamental motivation is that couplings among successive dilute layers at constant spacing offers the best hope for a future precise probing of the magnetic response function.

Given the severity of the geometrical and physical constraints suffered by the thinnest films, the effect on the magnetism appears remarkably mild down to monolayer film thicknesses. This is the point made in sect. 1 that the magnetism is generally robust. In reviewing these facts we first present relevant results for several metals, together with brief assessments in the light of the available theoretical modeling. The connection between these separate bodies of information is not fully formulated at the time of writing because the development of the subject matter is in its infancy.

4.3.1. Gadolinium

This is an interesting metal for the way the thin film tends towards bulk behavior at large thickness and to the two dimensional limit at dilute coverage. Bulk Gd has its axis of easy magnetization along c (see sect. 2) but the spin moment is canted from c by a large and temperature-dependent angle. There is only short-range order on a 0.1 μ m scale in the basal plane. No accepted explanation of this behavior is available, but d states that couple to both the 4f moment and the lattice may be responsible.

In thin films the demagnetizing factor, which favors basal plane magnetization, overcomes the c-axis bias of the bulk, and gives rise to easy alignment *in* the basal plane rather than perpendicular along c. Neither the film thickness nor the way this crossover takes place has ever been investigated. It may depend on the thickness d of the film relative to the correlation length of the in-plane bulk order.

Further changes caused by interfacial effects and reduced dimensionality may be anticipated as d is decreased to monolayer levels, even when the environment remains nonmagnetic but lanthanide-like. The fact that the thinnest films have spins oriented in the growth plane make them candidates for description by the XY model. Like the Heisenberg model, theory predicts that no true long-range order exists even down to 0K for interacting systems of XY symmetry, although a Kosterlitz–Thouless transition is expected (Kosterlitz and Thouless 1973). These predictions have been difficult to test in practice because the magnetic dilution of 2D systems causes the signals to fall below



Fig. 12. (a) Temperature dependence of the basal-plane magnetization of Gd films of various thickness. The applied field is 50 Oe in each case; (b) the thickness dependences of the Curie–Weiss temperature T_p and spin-glass temperature T_e . At low coverage, both temperatures increase as powers of the film thickness.

the detection level of steady state measurements (Falicov et al. 1990). The lanthanides have localized moments and interactions that can be parameterized simply in a way that resembles the simplified theoretical models. Also, MBE offers a means for preparing materials with many high quality layers of tailored structure spaced by a distance that exceeds the interaction range. Therefore the changes of magnetic behavior that occur as the Gd in rare-earth multilayers is reduced to monolayer thickness is of fundamental interest. From measurements of ac susceptibility Fahrle and Lewis (1994) have reported that Gd grown on W(110) has lost its ferromagnetism at a thickness of 7ML, while Li et al. (1993) find even a single Gd monolayer to be ordered.

The introduction by Tsui, Han, and Flynn of methods that allow the magnetism of rare earths grown on artificial mica to be probed down to the submonolayer level provides new opportunities for the study of 2D effects (Tsui et al. 1993b). Figure 12a from Tsui, Park and Flynn (1995) shows the magnetization produced by a 50 Oe field as a function of Gd film thickness and temperature. Even in the 2ML thick film the Gd magnetization approaches saturation at temperatures close to the bulk T_c of 290 K. This displays the robustness in a remarkable degree. Films 1ML and less in thickness exhibit markedly reduced fractional magnetizations which pass through a maximum at a lower temperature T_g . It will become evident below that this is associated with the spin glass behavior. Near 1ML coverage there is a well defined change from saturation magnetizations.

In the light of theory (Stanley 1971) it is natural to interpret the behavior using scaling arguments that lead to the following predictions for the dependence of M on H and T:

$$M \approx \left(1 - \frac{T}{T_{\rm C}}\right)^{\beta}; \qquad M \approx H^{-1/\delta}.$$
 (15)

Here the exponents β and δ are model dependent and hence offer valuable interpretation. Figure 12b shows how critical temperatures vary with Gd coverage down to 0.1ML. Values of δ obtained from the slopes of these curves may now be compared with theoretical predictions for various models and dimensionality.

It will suffice here merely to summarize the information obtained from studies of δ as a function of temperature and coverage. The two conditions of particular interest for each coverage are the ordering temperature and the temperature range well below it. Near the ordering temperature the values of δ at 5ML, 2ML and 1ML of Gd are about 3, 2.5 and 2, which correspond respectively to theoretical predictions for the 3D ferromagnet, the 3D random-axis magnet (RMA, to be described below) and the 2D RMA at T_c . Below $T_{\rm c}$ the values for the 2ML and 1ML coverages are about 6 and 3. These are again almost identical with the 3D and 2D RMA values of 5 and 3, while for 5ML coverage δ diverges as expected for a 3D ferromagnet below T_c . More detailed analysis reveals that the Gd thin layers follow both the full scaling equation and the phase diagram of the RMA; for details the reader is referred to the original paper (Tsui et al. 1995). In effect these results give the following single, consistent description of the thin-film limit. Instead of passing from 3D to 2D magnetic behavior with decreasing coverage, Gd transforms at 2ML coverage into a 3D random-axis magnet. The transition to 2D, which occurs between 2ML and 1ML takes the system to a 2D random-axis magnet. In this way the Gd avoids any transition to a 2D system of purely interacting spins.

These formerly unexpected results for the Gd thin-film limit may be understood as follows. The theory of the RMA (Aharony and Pytte 1980, 1983, Goldschmidt and Aharony 1985) includes in the Hamiltonian a weak interaction that is site-dependent and randomly oriented, in addition to the exchange interaction among spins. The model fits the observations, and its physical basis therefore requires identification. In submonolayer films the magnetic Gd and nonmagnetic Y atoms are laid down as an alloy and almost randomly. In addition they have different sizes and the admixture therefore contributes a geometrical anisotropy at Gd sites. While the Gd f^7 core is an S state ion and therefore isotropic, its magnetism nevertheless couples strongly to the axial crystal field in pure Gd as described above, presumably through valence electrons. It is likely that this same mechanism couples the Gd spins to the random alloy environment of the thin-film limit in a similar way. This random coupling breaks the symmetry of the exchange coupling and quenches the magnetism into a spin glass at low temperature.

4.3.2. Other lanthanides

The perturbation of bulk Dy and Er must be regarded as substantial whenever the film thickness falls well below the helimagnetic wavelength of about 30 Å. At that point the

distinctions between oscillatory and ferromagnetic phases become progressively blurred, and it vanishes altogether for *c*-axis monolayers. As a result, the role of magnetostriction in distinguishing between the energetics of phases that possess the different types of order must also be lost. It is thus of interest that the interactions among the spins of the three metals Gd, Dy and Er, as measured by the upper ordering temperatures of the three types of film, remain essentially unmodified as the film thickness is decreased to 2ML. Data for Er that establish this fact are shown in the inset of fig. 13. Without doubt this points to the dominance of interactions *within* the basal plane in determining the onset of order. Interplanar coupling is a weak interaction, although of critical importance for phase structure.

Several factors enter into a complete description of the magnetic states of Dy and Er as the film thickness is reduced through the few-monolayer regime. One can argue that Dy is not ferromagnetic on any rigid substrate: stretching on Y suppresses the ferromagnetic phase, while compression on Lu creates a domain structure that resembles a spin glass as the film thickness approaches 1ML. Er is still less able to accommodate the magnetostriction of the ferromagnetic phase, owing to its perpendicular polarization. These factors must be set beside the progressive blurring of the symmetry distinction between the competing phases as the thickness is reduced below the wavelength. A more quantitative discussion of the magnetic state is provided by scaling theory, just as for the case of Gd.

Their large magnetostrictions upon spin alignment indicate that the spins of Dy and Er couple more strongly than Gd to an anisotropic environment. At the same time their exchange couplings, as estimated from the ordering temperatures are, if anything, weaker than that for Gd. Therefore it may be anticipated that Er and Dy in Y (or any other host) must also conform to a RMA Hamiltonian in the limit when the thickness falls below 1ML. The force of this result is strongest for Er. With perpendicular polarization giving an Ising-like spin Hamiltonian, Er is predicted to remain ferromagnetic in the 2D limit. An added RMA coupling dramatically changes this prediction to a spin glass rather than ferromagnetic phase. An XY model of Dy does not order even at 0K, and the addition of random-axis fields produces a spin glass. The experimental observations lend strong support to these interpretations. Figure 13b compares the magnetization curves of Gd, Dy and Er thin layers in Y. The marked similarities among the S shaped curves arise from the fact that they all conform to a power law form. Equally of interest are the relative ordering temperatures T_p/T , shown in the inset for the three systems as functions of coverage. The three systems exhibit remarkably similar behavior. Furthermore the sharpness of the changes over the first 2ML of coverage suggests that the structure of the films must be smooth, with equally abrupt interfaces. Much of the data described here is as yet available only in the theses of Drs. F. Tsui (1992) and B. Park (1994) and their permission to include these materials here is gratefully acknowledged.

While the exploration of the thin-film limit of the lanthanides is in its early stages, several points emerge as worthy of further note. First is that the available detailed results are from films grown on mica. While the results are sharply structured on a monolayer



Fig. 13. (a) Thickness dependence of the Curie–Weiss temperature T_p , the extrapolated transition temperature T_c , the irreversibility temperature T_i , and the glass temperature T_g for thin Er films on Y. Data are shown on a logarithmic coverage scale, and reveal the rapid change of magnetic behavior in the 1–3ML range of coverage; (b) magnetic hysteresis for monolayer Gd, Dy, and Er grown on Y and Lu. Inset: normalized upper characteristic temperature T_p for Gd (circles) and Dy (diamonds) and T_i for Er (squares) shown as functions of rare-earth coverage in ML.

thickness scale, and this lends credence to a belief that the structures are good, it is nevertheless true that the films remain poorly characterized. Second, random-axis effects appear in retrospect as a natural result of alloying at the lowest (submonolayer) coverages, and as equally reasonable consequence of interfacial roughness and interdiffusion on the monolayer scale in films of thickness say 1–3ML. Whether or not it will prove possible to avoid these effects in films of precise 1ML and 2ML thickness grown on very wide terraces without interdiffusion is a matter for future research. One thing already apparent is that it will remain difficult to probe the exchange Hamiltonian by measuring the coupling between successive monolayer films until films lacking RMA effects can be prepared. Similar difficulties may restrict future fundamental studies of the fluctuation phenomena of coupled thin layers.

5. Superlattices

The rare-earth superlattices of interest here are composed of alternating blocks of two elements, grown in the epitaxial crystal regime (see sect. 4.1). Most superlattices studied to date are composed of alternating magnetic/nonmagnetic layers, although more complex structures involving two lanthanides have been studied recently. To a large extent, the magnetic properties of the superlattice mirror those of the epitaxial crystals of which they are composed, with the same sensitivity to epitaxial strain and clamping, and the same robustness of the lanthanide magnetic structures. One new aspect is the possibility of coherent coupling between successive magnetic blocks through the mediation of the intervening non-magnetic layers and the way the two band structures merge to define a single Q. In the case of lanthanide/lanthanide superlattices, the coupling among spins at opposite sides of an interface and its relation to the combined band structures adds further novel features, as does the interplay of differing transition temperatures and different easy magnetic axes.

The first observation of exchange coupling through non-magnetic spacers was reported by Kwo and coworkers (Kwo et al. 1985a,b, Majkrzak et al. 1986) who reported that epitaxial crystal layers of Gd, separated by varying thicknesses of Y, alternated between parallel and antiparallel alignment of their magnetization as a function of the Y-layer thickness. Such alternation has now been found in many cases, mostly involving transition metals with various non-magnetic spacers (Grünberg et al. 1986, Parkin 1991). A richer structure was discovered by the present authors and coworkers (Salamon et al. 1986) in Dy/Y superlattices, in which helimagnetic order propagates through Y layers as thick as 100 Å. Because the handedness, as well as the phase, of the helix is propagated, it follows that a helical wave must be induced in the intervening Y layer. The next section describes how the pitch of that induced helical wave can be deduced from neutron diffraction data.

As in the case of isolated epitaxial crystals, long-range order in superlattice structures occurs close to the bulk ordering temperature. One can thus infer that the exchange coupling provided by the spacer layers does *not* determine the ordering of the individual magnetic blocks, but serves rather to bring the magnetic order of individual epitaxial crystals into coherence. For helimagnetic (and longitudinally modulated) order, it is the coherence length of the ordered state that varies with the thickness of the spacer. This length, which can be deduced from the neutron data, falls rapidly with spacer-layer thickness, becoming equal to the magnetic-layer thickness in the limit of large separation. We will return to the question of interlayer coupling and coherence in sect. 5.3, after reviewing the properties of superlattices examined to date.

5.1. Magnetic scattering from superlattices

As in the case of the lanthanide elements and their alloys, neutron scattering has played a key role in determining the magnetic structures of rare-earth superlattices. Here the situation is complicated considerably by the interplay of chemical modulation, lattice strain, and magnetic order. Even the "rectangular wave model" of a superlattice, with perfectly abrupt interfaces and no lattice mismatch, Erwin et al. (1987), yields a complicated neutron scattering spectrum. In this simplified picture, the superlattice consists of N bilayers, each composed of N_R atomic planes of the lanthanide element with lattice spacing c_R and neutron scattering length b_R , and N_A planes of a non-magnetic element with lattice spacing c_A and scattering length b_A . The superlattice periodicity, defined as $\Lambda = (N_R c_R + N_A c_A)$, determines the spacing of allowed Bragg peaks, while the content of the superlattice unit cell sets the amplitude of these peaks via the structure factor $S_{nuc}(\kappa)$. The observed intensity due to nuclear (non-magnetic) scattering, for scattering wavevector κ along the growth direction, is given by

$$I_{\rm nuc}(\kappa_z) \propto \frac{\sin^2(\frac{1}{2}N\kappa_z\Lambda)}{\sin^2(\frac{1}{2}\kappa_z\Lambda)} S_{\rm nuc}(\kappa_z),\tag{16}$$

where

$$S_{\rm nuc}(\kappa) = b_{\rm R}^2 \frac{\sin^2(\frac{1}{2}N_{\rm R}\kappa_z c_{\rm R})}{\sin^2(\frac{1}{2}\kappa_z c_{\rm R})} + b_{\rm A}^2 \frac{\sin^2(\frac{1}{2}N_{\rm A}\kappa_z c_{\rm A})}{\sin^2(\frac{1}{2}\kappa_z c_{\rm A})} + 2b_{\rm A}b_{\rm R}\cos(\frac{1}{2}\kappa_z \Lambda)\frac{\sin(\frac{1}{2}N_{\rm A}\kappa_z c_{\rm A})\sin(\frac{1}{2}N_{\rm R}\kappa_z c_{\rm R})}{\sin(\frac{1}{2}\kappa_z c_{\rm A})\sin(\frac{1}{2}\kappa_z c_{\rm R})}.$$
(17)

The nuclear scattering profile predicted by this model is given in fig. 14 (solid lines) for 30 bilayers with $N_R = N_A = 3$, $c_A = 1$, $c_R = 1.1$, and $b_R/b_A = 1.5$. The main peak is located at $\kappa_z = 4\pi/c_{av}$, where $c_{av} = (N_R c_R + N_A c_A)/(N_R + N_A)$, corresponding to the (0004) peak of a *c*-axis, hexagonal superlattice. Subsidiary peaks are separated from the main peak by multiples of $2\pi/\Lambda$, and are termed "superlattice harmonics". The "envelope" function (17) is shown as a dashed line. The fine structure, due to the finite number of bilayers, has never been observed in practice. The same form is expected for X-ray diffraction, with the atomic form factors substituted for the scattering lengths. For comparison, we show in fig. 15 X-ray diffraction scans near the (0004) peaks of two Dy/Lu superlattices taken on the X14a beam line at NSLS. The broad peak just above 4.5 Å⁻¹ arises from Lu base and capping layers. A weak peak indexable as Lu₂O₃ is visible in the lower curve. There is a factor three difference in the lattice constant between the model of fig. 14 and the data of fig. 15; Λ is also longer for both samples in fig. 15.

The fundamental issue for the magnetic structure of superlattices is the existence or absence of long-range magnetic order. In sect. 2 we considered the case of transverse helimagnetic order with wavevector Q_z , for which satellites appear at positions separated from the main Bragg peak by $\pm Q_z$. In superlattices exhibiting long-range order, even



Fig. 14. Calculated scattering intensity in the rectangular-wave model, eqs. (16) and (17), with $N_R = N_A = 3$; $c_A = 1$; $c_R = 1.1$; $b_R/b_A = 1.5$. The solid line is the intensity calculated from eq. (16); the dashed curve is the structure factor given by eq. (17).

though the magnetic moments may be confined to a single component of the system (e.g. the lanthanide element), the corresponding planes in successive rare-earth blocks maintain a definite phase relationship. We denote the total phase advance across a single bilayer (modulo 2π) by Φ and assume that $N_{\rm m}$ successive bilayers have the same phase advance. Magnetic scattering peaks then appear not only as satellites of the main Bragg peak, separated from it by $\pm \Phi/\Lambda$, but also as satellites of the superlattice harmonics. In short, the magnetic scattering replicates the nuclear scattering peaks, but shifted by the effective magnetic wavevector $Q_{\rm eff} = \Phi/\Lambda$. If the lanthanide atoms alone are magnetic, the rectangular-wave model gives (Erwin et al. 1987)

$$I_{\rm mag}(\kappa_z)^{\pm} \propto \left(1 - \widehat{\kappa}_z^2\right) \left\langle J_z^{\rm R} \right\rangle^2 \frac{\sin^2(\frac{1}{2}N_{\rm m}\Lambda(\kappa_z \pm Q_{\rm eff}))}{\sin^2(\frac{1}{2}\Lambda(\kappa \pm Q_{\rm eff}))} S_{\rm mag}^{\pm}(\kappa), \tag{18}$$

where

$$S_{\text{mag}}^{\pm}(\kappa_z) = F_{\text{R}}^2(\kappa) \frac{\sin^2(\frac{1}{2}N_{\text{R}}(\kappa_z \pm Q_{\text{R}})c_{\text{R}})}{\sin^2(\frac{1}{2}(\kappa_z \pm Q_{\text{R}})c_{\text{R}})}.$$
(19)

Here, $\langle J_z^R \rangle$ is the amplitude of the lanthanide moment, $F_R(\kappa)$ is the magnetic form factor, and Q_R is the modulation wavevector in the lanthanide block. Note that the width of the magnetic Bragg peaks, as in the structural case, is given by $\Delta \kappa_z \simeq 2\pi/N_m \Lambda$.



Fig. 15. X-ray scans around the (0004) Bragg peak of two Dy/Lu superlattices.

Therefore, the width of the individual peaks is a measure of the number of bilayers that scatter coherently, or equivalently, the magnetic coherence length $\xi_m = N_m \Lambda$. In fig. 16, the nuclear and superlattice intensities are superposed for the structure of fig. 14, and with $\Phi = 4.5\pi$ and $Q_R c_R = 0.79\pi$. The assumptions of the rectangular wave model are summarized in fig. 17. Figure 18 shows the development of magnetic peaks in an Er/Y superlattice (Borchers et al. 1991). In this case, the z-component of the magnetization alternates in sign with a periodicity described by Q_z . Because of the polarization factors in the magnetic neutron scattering cross section, it is necessary to observe these peaks in the vicinity of the (1010) reflection.

The rich structure of superlattice harmonics predicted by the rectangular model is mirrored by the superlattice peaks observed in the Dy/Lu sample of fig. 15. At the opposite extreme, when only a sinusoidal modulation of composition exists, a single



Fig. 16. Superposition of nuclear (dotted) and magnetic (solid) intensities in the rectangular-wave model, eqs. (13) and (14). The nuclear peaks are those of fig. 14; the magnetic peaks have $\Phi = 4.5\pi$ and $Q_R c_R = 0.79\pi$.



Fig. 17. Schematic diagram of the rectangular wave model, showing (from top to bottom) the modulation of c-axis lattice spacing, the scattering factor, the turn angle, and the resulting total phase advance.



Fig. 18. Neutron scattering data for an Er/Y superlattice showing the development of magnetic order as the temperature decreases (cf. fig. 4 for a Er film).

superlattice harmonic can be observed. An analysis of the way the intensity varies with the order of the harmonic provides a measure of the sharpness of the chemical, structural, and magnetic changes at the interfaces (actually the Fourier transform). Two approaches have been used to improve on the rectangular-wave model: (i) modelling the rectangular waveforms of fig. 17 by means of error functions (Majkrzak et al. 1986) and (ii) suppressing the *m*th Fourier component of the rectangular wave by the factor $\exp(-\alpha m^2)$, termed the "diffusion model" (Erwin et al. 1987). In each case, a separate parameter (Gaussian width or exponential factor) is used to model the variation in composition, lattice spacing, and magnetic phase angle at each lattice plane, and each



Fig. 19. Real space variation of the lattice parameter and composition for the Dy/Lu superlattice, using the X-ray data of fig. 15.

provides a continuum between the ideal rectangular wave and a homogeneous alloy. In the diffusion model, for example, the magnetic phase angle at lattice plane j within a bilayer block can be written in terms of the turn angles ω_R and ω_A of the two components, as

$$\phi(j) = \frac{\Phi}{N_{\rm R} + N_{\rm A}} + \frac{\omega_{\rm R} - \omega_{\rm A}}{\pi} \sum_{i=0}^{j-1} \sum_{m=0}^{m=\infty} e^{-\gamma m^2} \frac{1}{m} \left[\sin\left(\frac{2\pi mi}{N_{\rm R} + N_{\rm A}}\right) - \sin\left(\frac{2\pi m(i - N_{\rm R})}{N_{\rm R} + N_{\rm A}}\right) \right].$$

$$(20)$$

Expressions such as this interpolate between the perfect rectangular model $(\gamma=0)$ and an alloy $(\gamma \rightarrow \infty)$. Figure 19 shows the result of a diffusion model analysis (Beach et al. 1993b) for a Dy/Lu superlattice, using X-ray data to determine the Dy composition and lattice spacing.

C.P. FLYNN and M.B. SALAMON

number of atomic planes							
Gd	Dy	Но	Er	Y	Lu	Number of bilayers	References
10				10		225	Majkrzak et al. 1986
10				6		189	Majkrzak et al. 1986
10				20		100	Majkrzak et al. 1986
5				5, 10		Fib.	Majkrzak et al. 1991
21				21		40	Vettier et al. 1986
5				5, 11		225	Majkrzak et al. 1991
	15			14		64	Salamon et al. 1986; Erwin et al. 1987
	16			20		89	Rhyne et al. 1987; Borchers et al. 1987
	16			9		100	Rhyne et al. 1987; Borchers et al. 1987
	14			34		74	Rhyne et al. 1988
	6			14		140	Salamon et al. 1992b
		27		3			Majkrzak et al. 1988
		15		3			Majkrzak et al. 1988
		14		13			Majkrzak et al. 1988
		20			15		McMorrow et al. 1993
		40			15		McMorrow et al. 1993
			23	19		100	Borchers et al. 1988a,b; Erwin et al. 1988a
			32	21			Erwin et al. 1988a
			13	26			Erwin et al. 1988a,b
	14				5	80	Beach 1992
	14				8	70	Beach 1992
	14				20	80	Beach et al. 1992
	14				30	40	Beach 1992
	15				15	40	Beach 1992
	16				20	60	Beach 1992
	18				22	40	Beach 1992
	21				11	70	Beach 1992
		40	13				Simpson et al. 1994
		10	23				Simpson et al. 1994
5	10						Majkrzak et al. 1988

Table 1 Superlattices characterized magnetically and by neutron diffraction. The entries in the element columns are the number of atomic planes

5.2. Superlattice ordering

The synthesis of a perfectly coherent magnetic/nonmagnetic superlattice structure does not, of course, guarantee that long-range magnetic ordering will occur. Yet, in a surprisingly large number of cases, long-range order does in fact arise. As described above, two basic types are observed: (i) parallel or antiparallel stacking of ferromagnetic lanthanide (and iron-group) blocks; and (ii) propagation of helimagnetic or sinusoidal magnetization through many bilayers. Table 1 summarizes the structures that have been realized.

5.2.1. c-axis samples

Most rare-earth superlattice samples studied to date have been grown along the (0001) direction, or *c*-axis (Flynn et al. 1989a, Falicov et al. 1990). While MBE growth is more straightforward in this orientation, it is also convenient to have the chemical and magnetic modulation in the same direction.

5.2.1.1. Gd/Y superlattices. The Gd/Y system was one of the first rare-earth superlattices to be grown and studied, and was the first system in which alternation of the sign of the coupling across a non-magnetic spacer layer was observed (Kwo et al. 1987). As in the epitaxial crystal regime, the Gd magnetization lies in the basal plane, where the



Fig. 20. Oscillation of the remanent magnetization and saturation magnetic field for Gd/Y superlattices (from Kwo et al. 1985a).

Fig. 21. Neutron scattering data from an antiferromagnetically aligned Gd/Y superlattice. Odd-numbered peaks arise from magnetic scattering (from Majkrzak et al. 1986).

demagnetization field overwhelms the weak c-axis anisotropy. This is made evident by the oscillatory dependence of the coercive field on Y spacer-layer thickness, with a period of seven Y layers (fig. 20). Note that the remanent magnetization is large when the coercive field is small. The interplanar antiferromagnetic exchange energy may be estimated from $J_{\rm af} = H_{\rm s} M t/4$ (Parkin 1991) where t is the Gd-layer thickness; the value $J_{\rm af} \approx 0.6$ erg/cm is similar to values obtained for the coupling or transition metal blocks across, e.g. Cu. The conventional explanation (Yafet 1987a) is that the coupling arises from the same RKKYlike mechanism, described in sect. 2.1, and predicts the 7-plane period (approximately 50° per Y layer) in agreement with the susceptibility peak in fig. 1. Neutron scattering studies confirm that the magnetic structure of the superlattices that possess the maximal coercive fields consists of ferromagnetic Gd blocks, with blocks in adjacent bilayers oppositely aligned (Majkrzak et al. 1986). Additional magnetic peaks in neutron scattering (indexed with odd integers in fig. 21) lie exactly between the superlattice harmonics (even indices) as expected from doubling the superlattice periodicity. This was the first definitive demonstration of oscillatory exchange coupling, which has subsequently been observed in a wide range of magnetic/nonmagnetic superlattices and multilayers. Results on Gd/Y have been extensively reviewed by Majkrzak et al. (1991).

5.2.1.2. Dy/Y superlattices. The first superlattice system to show non-trivial long-range order was a sample denoted $[Dy_{17}|Y_{14}]_{64}$, consisting of 64 bilayers, each composed of a Dy block of 17 atomic planes (8.5 hexagonal unit cells thick) and an Y block of 14 (7 hexagonal cells thick) (Salamon et al. 1986). Helimagnetic satellites, which first appear at 160 K, close to the ordering temperature of bulk Dy, persist down to the lowest temperatures studied (~10 K). As discussed in sect. 4.1, the suppression of the ferromagnetic transition is a consequence of epitaxy, and does not originate uniquely from the superlattice structure.

A number of similar *c*-axis samples were subsequently prepared and studied (Salamon et al. 1991, 1992a, Erwin et al. 1987, Rhyne et al. 1989). Typical neutron scattering data are shown in fig. 22. Note the constancy of both the main nuclear Bragg peak (~2.2 Å⁻¹) and the superlattice harmonic ($\simeq 2.25 \text{ Å}^{-1}$). Ferromagnetic order, were it to appear, would add magnetic scattering intensity to those peaks. At 6K, the widths of the magnetic peaks are comparable to those of the nuclear peaks, demonstrating that the magnetic and structural coherence are comparable. The increasing intensity and changes in relative intensity of the central and superlattice harmonic *magnetic* peaks result from the interplay of the mismatch between c_{Dy} and c_{Y} with the changing value of Q_{Dy} . From data sets such as these, it is possible to extract the temperature dependence of the turn angle for Dy and (modulo $2\pi/N_{\rm Y}$) the effective turn angle in the Y. The result of such an analysis is shown in fig. 23 (Rhyne et al. 1987). The general result is that the turn angles observed in superlattice structures are larger than in elemental Dy at all temperatures below $T_{\rm N}$, and that the Y layers exhibit an effective turn angle of ~50°/plane, which is close to that observed in dilute YDy alloys. It is not surprising that the Dy turn angles are larger in superlattices; atomic planes near the interfaces lack further-neighbor atomic planes whose antiferromagnetic coupling determines the pitch of the helix. This justifies our



Fig. 22. Neutron scattering data from a Dy/Y superlattice. The intensity of the main Bragg peak is constant to 6 K, ruling out the development of ferromagnetic order.

assertion that interlayer coupling slightly perturbs the magnetic properties of the epitaxial crystalline blocks of which the superlattice is composed.

The absence of further-neighbor planes also induces some residual ferromagnetic order within each Dy block, but this is not coherent from bilayer to bilayer. Thus, in fig. 24 (Rhyne et al. 1989), the moment calculated from the coherent helical Bragg peaks falls below the expected $10\mu_B$ per Dy atom. The fact that the missing intensity appears as a broad feature centered on the nuclear Bragg positions indicates the presence of short-range, incoherent ferromagnetic order in each bilayer.



Fig. 23. Temperature dependence of the turn angle in Dy and Y layers as a function of temperature for several superlattices.

The propagation of helimagnetic order through non-magnetic vttrium layers is a more elaborate process than that which couples ferromagnetic Gd blocks in Gd/Y superlattices. Not only must the yttrium transmit the relative orientation of spins at the interfaces, but also the handedness (chirality) of the helix in each block. Consequently, the helical coherence that develops within each Dy block must influence the handedness of its neighbors. Yafet et al. (1988) superposed the RKKY-like oscillations of pairs of Dy planes to model helical coupling, arguing that due to band-matching only interfacial layers need be considered. The situation is quite different from that in dilute alloys, where the ordering temperature decreases with decreasing Dy concentration. We have seen in sect. 4.1 that thin Dy layers order at the bulk Néel temperature. The issue for coherent order rests on whether the indirect exchange coupling via the Y is sufficiently strong to induce the same chirality in successive Dy blocks. Because some helical order is required, and because anisotropy barriers grow as the order increases, there will be an increasing tendency to develop "chiral stacking faults" as the exchange coupling is reduced. This is reflected in a reduction in the number of bilayers that contribute coherently, and consequently to a broadening of the magnetic peaks observed in neutron scattering. We can define the



Fig. 24. Magnetic moment per Dy atom for a Dy/Y superlattice (a) deduced from the helimagnetic peaks; (b) shows that a residual, incoherent ferromagnetic intensity is present, accounting for the "missing" moment.

magnetic coherence x length in terms of a magnetic peak width through $\xi_{\rm m} = 2\pi/\Delta\kappa_{\rm mag}$, where $\Delta\kappa_{\rm mag} = (\Delta\kappa_{\rm obs}^2 - \Delta\kappa_{\rm nuc}^2)^{1/2}$, $\Delta\kappa_{\rm obs}$ is the measured width of the magnetic peak, and $\Delta\kappa_{\rm nuc}$ is the width of a nuclear Bragg peak. This definition is employed to deconvolute the structural and magnetic coherence. A plot of the magnetic coherence length vs the inverse of the thickness t of the yttrium block is shown in fig. 25 (Rhyne et al. 1989). At an extrapolated thickness of 140 Å, helimagnetic order is confined to single



Fig. 25. Magnetic coherence length vs the inverse of the Y layer spacing. Dy layers are decoupled when the Y-layer thickness exceeds 140 Å.

Dy blocks. We emphasize again that, unlike the case of alloys, the Néel temperature remains high as the Y fraction increases; only the coherence in the growth direction is lost.

The low-temperature ferromagnetic phase of Dy can be induced by relatively modest magnetic fields applied along the easy axis in the basal plane. Neutron scattering data (Rhyne et al. 1989, Salamon et al. 1992a) on $[Dy_{16}Y_{19}]_{89}$ in fig. 26 show at 10K that as the helimagnetic state collapses abruptly between 5 kOe and 10 kOe, the magnetic scattering intensity reappears in the structural Bragg peak and its superlattice harmonics; these are indicators of long-range ferromagnetism. At 130 K, the transition is more gradual, and it occurs through the loss of coherence of the spiral, and the coexistence of helimagnetic and ferromagnetic states. When the field is reduced to zero after saturation, the helical phase reappears at 130 K in all samples, but not at 10 K. Figure 27 shows the behavior of the *c*-axis lattice parameter of $[Dy_{15}Y_{14}]_{64}$ as a function of applied field (Erwin et al. 1987). As the sample is magnetized, the *c*-axis increases in length by 0.1%, approximately one-half of the change that accompanies ferromagnetic order in the bulk. The larger lattice parameter persists when the field is



Fig. 26. Evolution of the helimagnetic peaks in a field for a Dy/Y superlattice at 10K and at 130K. Note loss of coherence at 130K.

subsequently reduced to zero at 10 K. On warming above 130 K, the fully coherent helical phase returns, and the lattice parameter returns to its original value. It is clear that a substantial fraction of the magnetoelastic distortion that accompanies ferromagnetism in



Fig. 27. (a) Temperature dependence of the field cooled (FC), zero field cooled (ZFC) and saturated values of the *c*-axis lattice parameter of a Dy/Y superlattice; (b) cycling the field at 10 K leaves the lattice parameter in its expanded state; at 130 K, the change is reversible.

Dy is realized in the superlattices, despite the constraints imposed by epitaxy (Erwin et al. 1989, 1990).

5.2.1.3. *Ho/Y superlattices*. Ho/Y superlattices have since been grown and studied by neutron (Bohr et al. 1989) and magnetic X-ray diffraction (Majkrzak et al. 1991). A coherent basal plane spiral forms, as in Dy/Y, with coherence extended over many bilayers. Analysis of the turn angles of the separate blocks also yields 51° /Y layer, and a temperature-dependent turn angle in the Ho layer that is significantly larger and less temperature dependent than that of bulk Ho. Unlike the Dy/Y case, higher-order harmonics were observed in a $[Ho_{40}|Y_{15}]_{50}$ superlattice, which indicates the existence of spin-slip structures. Fifth and seventh order harmonics were observed with an average turn angle of 40°/Ho plane. Jehan et al. (1993) suggest that this is evidence for a (2121) spin-slip sequence, a sequence not observed in bulk Ho, while Majkrzak et al. (1991) assume a purely antiferromagnetic coupling through the Y layers, and obtain stacking sequences similar to those observed in the bulk. To date, no field dependences have been reported for these superlattices.

5.2.1.4. Er/Y superlattices. As discussed in sect. 4.1.3 above, epitaxial Er films order in a sinusoidal, *c*-axis modulated (CAM) structure near 85 K, as in the bulk, but do not develop a conical phase. A helimagnetic component does appear, but only substantially below the temperature (20 K) at which it appears in the bulk. Therefore, Er/Y superlattices permit the study of longitudinal order propagating in the CAM phase, and with it the possibility that long-range magnetic coherence might be more readily achieved. There are two likely sources of long-range coupling: (i) the phase difference across an Y block



Fig. 28. Development of helimagnetic order in an Er/Y superlattice below 20 K as shown near (0002).

is always an even or odd multiple of π – basically the same as Gd/Y or, (ii) the phase is determined by the number of Y planes in the bilayer, and can take on any value. Neutron scattering data, similar to those shown in fig. 18, have been collected for a number of superlattices with Y spacer layers varying between 19 and 25 atomic planes (Borchers et al. 1991). The phase shift, modulo 2π , across the spacer layer ranges from 0.7π to 1.5π , and is consistent in every case with a phase advance of 51° per yttrium layer. The temperature independent intensity of the (1010) peak in fig. 18 demonstrates, as found for Dy/Y superlattices and thin Er films, that the low-temperature ferromagnetic transition of the bulk does not occur in the epitaxial system. Nonetheless, helimagnetic order does occur near 20 K, as is apparent in fig. 28. However, when it does appear, it is considerably less coherent than the CAM structure; the helimagnetic peaks are barely resolvable, even at 6 K.



Fig. 29. Temperature dependence of the turn angle in Er and Y layers for several superlattices. The solid line shows the turn-angle data for bulk Er.

Fig. 30. Néel temperatures for Er/Y superlattices (circles) and films (squares) vs the measured *c*-axis lattice parameter. The dashed line marks the *c*-axis spacing of bulk Er at 85 K.

We describe in sects. 2.2 and 4.1.3 how the magnetic structure of elemental Er, and to a lesser extent of thin epitaxial films, passes through a sequence of commensurate



Fig. 31. Magnetization curves for $[Er_{13,5}|Y_{25}]_{100}$ showing the appearance of a state of intermediate magnetization.

lock-in states, separated by discrete transitions. As fig. 29 shows, the turn angle of several Er/Y superlattices remains, to the contrary, nearly constant at $51-52^{\circ}$ per layer from 70 K to 6 K. While both films and superlattices are strained, and neither exhibits a spontaneous ferromagnetic phase, only the Néel temperature of the superlattices is significantly modified by strain. This is shown in fig. 30, where films and superlattices with the same *c*-axis lattice parameters (measured at room temperature) are seen to have significantly different transition temperatures (Borchers et al. 1991). It appears that the more two-dimensional nature of the superlattice components contributes to a lowering of the Néel temperature.

The magnetization process of Er/Y superlattices is much more complicated than that of Dy/Y owing to the sequence of commensurate lock-in states that are accessible. On application of a field, the turn angle measure by neutron scattering shifts abruptly from 50.3° to 51.4° per layer. The latter represents a phase in which an alternation of the *c*-axis modulated structure is completed in exactly 7 Er layers. This state, which has three downspin and four up-spin planes, has a net magnetic moment, and is stabilized by the applied field (Borchers 1990). This same 2/7 state was found to be favored in thin epitaxial films even in the absence of a field (cf. fig. 11). Other intermediate states have been observed in superlattices with differing Er-block thicknesses (Beach et al. 1990). The full saturation moment appears at a critical field H_c that is approximately 17 kOe at low temperatures, increasing to 30 kOe near 60 K for all superlattices studied. Magnetization curves for [Er_{13.5}]Y₂₅]₁₀₀, shown in fig. 31, reveal one such intermediate state, which appears at 40 K



Fig. 32. Neutron scattering data for the sample of fig. 31 in the intermediate state.

Fig. 33. Extrapolated T = 0 critical fields (expressed as an energy) for epitaxial Er thin films and multilayers. The dashed line is calculated from eq. (11).

with an internal magnetic field of $\simeq 23$ kOe (Borchers et al. 1988a). The neutron scattering patterns in fig. 32 for the same sample at 40 K, and in various fields, reveal a transition to a complex spin state near an *applied* field of 27 kOe (Borchers 1990). A tentative assignment of this structure to the alignment sequence $7\uparrow 3\downarrow 8\uparrow 3\downarrow$ gives a moment 9/15

of the saturation value and approximately the correct positions for the neutron scattering intensity.

Figure 10 demonstrates that the field H_c , required to drive epitaxial Er films into the cone phase, increases as the film thickness decreases. This trend continues in the superlattices. However, it is not layer thickness but rather the coherency strain ε_0 that appears in eq. (12). This is apparent in fig. 33 where the extrapolated T=0 value of H_c varies with the measured *c*-axis strain. The dashed line in that figure is obtained by equating the magnetic energy gained in the cone state to the sum of the magnetoelastic energy from eq. (11) and the exchange energy barrier. Values of the exchange energy, elastic constants, and magnetoelastic constants are those of bulk Er (Rosen et al. 1973).

5.2.1.5. Lu-based superlattices. Section 4.1.2 describes in detail the dramatic increase in the ferromagnetic transition temperature of thin Dy films (Beach et al. 1993b) grown on Lu. Nearly identical effects are observed in superlattices where the process can be studied in detail. Figure 34 shows how the magnetic order develops in $[Dy_{14}|Lu_8]_{70}$ (Beach et al. 1993a). Helimagnetic order appears near the bulk Néel temperature; the magnetic peaks shown here at 160K persist down to about 120K. At lower temperatures, the helimagnetic peaks gradually disappear and are replaced by increased intensity in the



Fig. 34. Neutron scattering data for a Dy/Lu superlattice showing the appearance of helimagnetic order below 170 K, which gives way to ferromagnetic order at low temperatures, evidenced by increased intensity of the Bragg peak at 2.23 Å⁻¹.



Fig. 35. Neutron scattering data for the Dy/Lu superlattice that develops antiferromagnetic stacking of ferromagnetic Dy blocks, signalled by the peaks marked with arrows.

Fig. 36. Temperature dependence of the Dy turn angle as a function of T/T_c , where T_c is the ferromagnetic Curie temperature. Shown are bulk Dy (line); a 400 Å film (triangles); $[Dy_{14}|Lu_5]$ (inverted triangles); $[Dy_{18}|Lu_{22}]$ (open circles); and $[Dy_{15}|Lu_{15}]$ (squares) and $[Dy_{14}|Lu_{30}]$ (solid circles).

Bragg peak and the superlattice harmonics, which indicates the formation of long-range *ferromagnetic* order. However, a sample with thicker Lu layers, $[Dy_{15}|Lu_{15}]_{40}$, exhibits an antiferromagnetic stacking of ferromagnetic blocks at low temperature (fig. 35), exactly as in the Gd/Y superlattice shown in fig. 21 (Majkrzak et al. 1986). Unlike the Gd/Y case,



Fig. 37. Approximate phase diagram for the Dy/Lu system.

however, samples with 9, 11, 15, 20, 22 and 30 Lu layers in the spacer block all exhibit antiparallel stacking at low temperatures (Beach 1992). Only the 8 Lu-layer and 5 Lu-layer samples exhibit ferromagnetic stacking. A greatly enhanced ferromagnetic transition temperature has also been reported recently for $[Dy_7|Zr_{11}]_{40}$, for which the tensile mismatch is 10%, based on magnetization data (Luche et al. 1993).

As in the case of Dy/Y shown in fig. 23, there is a definite dependence of the turn angle on relative layer thickness, and therefore on strain. Exploiting the thin-film result in fig. 7, we plot in fig. 36 the turn angle in the Dy component vs $T/T_{\rm C}$ and hence strain (Beach 1992). Interestingly, $\omega_{\rm Dy}$ for Dy/Lu superlattices and the 400 Å film, scale with bulk Dy, within experimental uncertainty. From these data we are able to construct the approximate phase diagram for Dy/Lu superlattices shown in fig. 37 (Beach 1992). This is an extension of the single-layer phase diagram of fig. 7.

Although it is not possible to follow the helical phase to low temperatures, we can still make an estimate of the coherence lengths at 160 K. These are shown in fig. 38, along with the coherence of the aligned and antialigned ferromagnetic phases as measured at low temperature. The magnetic coherence in these superlattices is clearly much smaller than in the Dy/Y system, which itself results from strains associated with the appearance of ferromagnetic order in a superlattice system.

As described in sect. 2.3, the driving energy for ferromagnetism in Dy and Er is magnetoelastic (Cooper 1972, Rhyne 1972). For Dy, the single-ion magnetoelastic energy is minimized in the ferromagnetic state, which results in an orthorhombic distortion of the hexagonal structure. How does this transition occur in a superlattice that remains clamped to its substrate? Figure 39 provides the answer through high resolution X-ray scans of the $(20\tilde{2}1)$ peak in the reciprocal lattice plane normal to the c^* -axis. In bulk Dy,



Fig. 38. Coherence lengths of the magnetic order in Dy/Lu vs Lu=layer thickness. Open circles, ferromagnetic alignment; solid circles, antiferromagnetic alignment; triangles, helimagnetic order.

Fig. 39. X-ray intensity contour maps of the plane $(h0\bar{h}1)$ near the $(10\bar{1}1)$ lattice point: (a) low temperature; (b) room temperature. The dotted lines are fits to a domain model as described in the text.

the unique *a*-axis increases in length by 0.2%, and this decreases the hexagonal angle by 0.2°. In a multidomain sample, each $(h0\bar{h}l)$ Bragg peak is split in three by the distortion. The contour maps in fig. 39 show the room-temperature and low-temperature intensity distribution (Beach et al. 1993a). The dashed curves in the left panel are calculated by placing three identical asymmetrical Gaussians at positions expected for an orthorhombic distortion. The splitting is approximately 60% of that for bulk Dy. The linewidths are quite large, corresponding to domains approximately 400 Å in diameter. At this size, the maximum atomic displacement within a domain is less than one-half of the lattice constant, which serves as a reasonable limit if no plastic deformation is to occur. The formation of these magnetoelastic domains is reversible; however, samples warmed to room temperature show some residual broadening that is not evident in samples that are subsequently aged for long periods (months).


Fig. 40. Destruction of the antiferromagnetic alignment of Dy layers in $[Dy_{21}[Lu_{11}]_{70}$ by an applied field. Note the metastability of the aligned state. Rem = remanent state.

Ho/Lu superlattices have been grown and studied by neutron diffraction (McMorrow et al. 1993). Ho layers composed of 10 or 20 atomic planes, separated by 17 atomic layers of Lu, order in a basal plane helix near 130 K, which persists to approximately 30 K. Below 30 K, an unusual phase develops, with ferromagnetic alignment in the basal plane, which is canted 30° out of the plane; the magnetization of successive Ho blocks is antiparallel.

The helimagnetic phase of Dy/Lu superlattices exists only over a narrow temperature range near T_N . On application of a relatively small magnetic field at 160 K, the coherence of the helix is lost; for $[Dy_{21}|Lu_{11}]_{70}$, a field of 1 kOe suffices to smear the helimagnetic peaks and shift magnetic intensity into the ferromagnetic peaks. At low temperatures, the antiparallel alignment of ferromagnetic Dy blocks is destroyed by an applied field. Figure 40 shows the shifting of magnetic intensity from antiferromagnetic peaks (e.g. at 2.2 Å⁻¹) to ferromagnetic positions (e.g. at 2.17 Å⁻¹). Note also that the antiparallel state



Fig. 41. Hysteresis loops for antialigned $[Dy_{16}|Lu_{21}]$ (open circles) and aligned $[Dy_{14}|Lu_8]$ (solid circles) superlattices showing remanent magnetization.



Fig. 42. Hysteresis loops for various Dy/Zr superlattices (from Luche et al. 1993).

does not recover after saturation at 10K (Beach 1992). The ferromagnetic remanence evident in fig. 40 can be readily observed in hysteresis loops. Loops for both $[Dy_{14}|Lu_8]_{70}$ (aligned blocks) and $[Dy_{16}|Lu_{20}]_{80}$ are shown in fig. 41. Similar data shown in fig. 42 for Dy/Zr, reveal analogous behavior but with much larger coercive fields (Luche et al. 1993).

5.2.1.6. Other superlattice structures. Recently, Dy/Sc and Nd/Y superlattices have been grown (Tsui et al. 1993a). Long-range structural coherence is achieved despite the 8% lattice mismatch in the former system. However, no magnetic order is observed at 160 K, and only short-range ferromagnetism can be detected at low temperatures. In a 60 kOe magnetic field at 10 K, the magnetic intensity appears on the Bragg peak and superlattice harmonics, and the broad, short-range peak disappears. These results are visible in the series of scans shown in fig. 43. The Nd/Y superlattices are the first to involve a light rare-earth element, and the first to mix dhcp (Nd) and hcp (Y) lattice types. This work is still in its early stage, and we defer further discussion (Everitt et al. 1995).

In addition to the simple superlattice structures described above, a number of more complex structures have been fabricated. They include Fibonacci sequences of Gd and Y (Majkrzak et al. 1991) and lanthanide/lanthanide superlattices with competing anisotropics, such as Ho/Er (Simpson et al. 1994), Gd/Dy, and Dy/YDy (Camley et al. 1990). We refer the reader to the original sources for details.



Fig. 43. Neutron scattering near the (002) peak for $[Dy_9]Sc_{14}]_{66}$: (a) 160 K; (b) 10 K; (c) 60 kOe field at 10 K.

5.2.2. a- and b-axis samples

It is clear from the previous sections that insertion of non-magnetic ab-plane layers does not preclude the appearance of long-range helimagnetic and c-axis modulated order. We infer that this arises because nesting features in the Fermi surfaces of the non-magnetic elements studied (Y and Lu) result in a magnetization wave surrounding substituted lanthanide atoms that decays slowly along the c-axis. However, the predicted absence of such features in the basal plane should cause a much more rapid decay of magnetization in those directions. It is possible (Du et al. 1988) to explore such effects through the fabrication of superlattice structures with the growth axis along either the crystalline aor b-axis, so that the helical axis lies in, rather than normal to, the growth plane.

5.2.2.1. *a-axis and b-axis Dy/Y.* As in the case of *c*-axis samples, magnetic neutron reflections should be centered at $[0002\pm\tau]$, where $\tau = Q_{\text{Dy}}c_{\text{Dy}}/2\pi$. For a superlattice grown along *b*, the superlattice harmonics are located a distance $2\pi/\Lambda$ from the principal Bragg reflections in the *a*^{*} direction (Flynn et al. 1989b, Tsui et al. 1991). However, no magnetic satellites of the superlattice harmonics are present, as seen in fig. 44. In these scans $\zeta=0$ corresponds to the *c*^{*}-axis. The sharp peaks are the superlattice harmonics, and the broad magnetic satellite shows no superlattice modulation. Hence, helical order appears with a well-defined turn-angle, but it is incoherent in successive bilayers. Figure 45 summarizes the temperature dependence of the turn angle for various *a*- and *b*-axis-grown samples, with *c*-axis-grown data plotted for comparison (Tsui 1992).



Fig. 44. Neutron scattering scans for a *b*-axis Dy/Y superlattice. Solid circles, scan through nuclear superlattice peaks; open circles, scan across the helimagnetic peak. The absence of sharp superlattice harmonics indicates that the order is confined to each Dy layer.



Fig. 46. (a) Schematic representation of $\mathcal{J}(q)$ and (b) its real-space envelope function. The inset in the foreground is the actual Fourier transform along c.

The absence of coupling for *a*-axis and *b*-axis superlattices can be understood within the RKKY model. The rapid rise and relatively flat-topped peak of the susceptibility $\chi_Y(q_z)$, as shown in fig. 1, give rise to long tails in the real space response. Figure 46a shows the exchange energy $\mathcal{J}(q)$ in the a^*-c^* plane, assuming that the sharp peak in the

susceptibility is independent of q_x . The attenuation in the a^* direction arises from the form factor $j_{sf}(q)$. The corresponding real space exchange interaction between two planes separated by a distance R is shown in fig. 46b. The actual oscillating function is sketched along the *c*-axis, while the envelope function J(R) is sketched in the b-c plane, which corresponds to the a^*-c^* plane in reciprocal space. A slow decrease in coupling with *c*-axis separation contrasts sharply with the rapid decrease in coupling along the *b*-axis. Further, as pointed out by Tsui (1992), Dy layers with the *c*-axis in the growth plane drive the Y layer at Q_{Dy} , which is off the peak in the Y susceptibility, further reducing the interaction.

5.2.2.2. *b-axis Gd/Y.* Gadolinium/yttrium superlattices were grown along the *a*-axis (Tsui 1992, Tsui et al. 1992) and are found to order as ferromagnetic blocks at $\simeq 290$ K, somewhat below the Curie temperature of bulk Gd. Just below T_C , all superlattices order with Gd blocks antiparallel; in *b*-axis [Gd₁₉|Y₈]₈₅, the Gd blocks switch to parallel alignment below 100 K. Figure 47 shows the dependence of the antiparallel (solid circles) and parallel (open circles) neutron peaks on applied field for the above sample. Note that



Fig. 47. Neutron scattering intensities of the ferromagnetic (open circles) and antiferromagnetic (solid circles) peaks for b-[Gd₁₉]Y₈]₈₅. The zerofield state is ferromagnetic.

the coercive fields are on the order of 50 Oe in the antiparallel alignment (at 200 K), in sharp contrast with the 5 kOe coercive field for $N_{\rm Y} = 8$ for c-axis Gd/Y as seen in fig. 20.

5.3. Interlayer coupling and long-range coherence

Previous sections describe how magnetic layers first develop intralayer order at the Néel temperature, and its insensitivity to film thickness and interfacial effects. Much interest, in the case of superlattices, attaches to the way these rare earth nanostructures develop and maintain long-range interlayer order. The process by which successive layers order is a good deal more delicate than the behavior of a single layer, as it is mediated by weak coupling through nonmagnetic spacers. Nonetheless, inter- and intraplane order develop together at the Néel temperature, without obvious temperature dependence of the coherence length either near or below the transition. It is interesting to compare the magnetic properties of the superlattices with other layered magnets, such as the series $(C_nH_{2n+1}NH_3)_2CuCl_4$ (Steiger et al. 1983). In that system, ferromagnetic CuCl₄ sheets are separated by organic molecules of increasing size. Up to n = 10, the Curie temperature remains close to that of the n=1 sample, while even for n=1, order is confined largely to a single plane, as evidenced by neutron scattering data which show a "ridge" of magnetic scattering rather than intensity localized near a Bragg peak. Many other "quasi-2D" magnetic materials show two-dimensional correlations over a wide temperature range before ordering three-dimensionally at the Néel or Curie point. Thus, the nature of magnetic ordering in the superlattices is unique, and at present there is little understanding of the energetics and kinetic processes by which quasi-long-range order is developed in these structures.

As is the case in lanthanide metals themselves, interlayer coupling must involve the polarization of conduction electrons within the non-magnetic spacers. To explain that process, Yafet (1987a) extended the RKKY mechanism (see sect. 2.1 and Appendix) by considering a pair of Gd monolayers embedded within an Y crystal. This treatment correctly predicts the alternating ferromagnetic and antiferromagnetic exchange coupling, but the inverse-square dependence of the coupling strength on the layer thickness (Yafet 1987b) is stronger than that observed ($\sim t^{-1}$). Such ideas have been extended to other systems, taking into account the detailed Fermi surface of the spacer element (Bruno and Chappert 1991, Herman et al. 1992). Helimagnetic coupling requires, at a minimum, the superposition of the RKKY oscillations of two monolayers in each of the coupled lanthanide epitaxial crystals (Yafet et al. 1988). However, exchange coupling between two metals is strongly affected by Fermi-surface matching conditions. If the interfaces are perfect, electron states in the two metals are coupled only if they have the same transverse crystal momenta; i.e, $k_{F\perp}^{A} = k_{F\perp}^{B}$, where A and B refer to the two metals. Because of the existence of interfacial potentials, the components parallel to the growth axes need not be conserved; i.e. $k_{F\parallel}^{A} \neq k_{F\parallel}^{B}$. Yafet et al. (1988) exploited this feature to justify considering only the outer one or two atomic planes of each magnetic layer. The band structure features of the lanthanides (and yttrium) that give rise to the peaks in fig. 1, are flat sheets normal to the c^* -axis located near the M-point. The separation between these sheets



Fig. 48. Calculated exchange coupling for Gd blocks of 10 and 6 atomic layers separated by varying numbers of Y layers.

determines Q, and is obviously different for the different elements. In *c*-axis superlattices involving Y or Lu, then, there is significant hybridization of those portions of the Fermi surface between the polarized lanthanide and unmagnetized Y or Lu bands, inducing a spin-density wave in these materials. This can occur because the flatness of the sheets ensures that states of the same transverse momentum exist in each metal. However, in *a*-and *b*-axis samples, the vector Q lies in the growth plane, and there is no hybridization of these portions of the bands between the two metals, and consequently no induced spin-density wave.

Calculations of interlayer exchange that take into account the complex band structures of the constituents are only now appearing. Xia and Chang (1992) have parameterized the bands of Gd and Y to obtain a superlattice tight-binding band. With this, they have calculated the non-local susceptibility, with it, the exchange coupling $J_{12}^{\alpha\beta}$ between Gd atoms in layer r_1 of block α and layer r_2 of an adjacent block β . The net interlayer coupling is then obtained by summing over all pairs of planes. The results for two Gd layers are shown in fig. 48; although incomplete, the approximately 7 Y-layer period can be discerned. Related arguments have been used by Mathon (1991) to explain the giant magnetoresistance effect in transition-metal multilayers in terms of localization of spinsubbands depending on the relative magnetization of neighboring ferromagnetic layers.

Even with a model for weak interlayer coupling there is, at present, no detailed explanation for the decrease in coherence with spacer-layer thickness t, as observed in superlattice structures (fig. 25), and also in the Er/Y system (Salamon et al. 1992b). To proceed, we make an analogy with the theory of random anisotropy in ferromagnets (Chudnovsky et al. 1986, Aharony and Pytte 1980, 1983, Goldschmidt and Aharony 1985). These models assume that the magnetic anisotropy field H_r changes direction

randomly over a distance R_a , which can be either a microscopic distance or the size of a crystalline grain. Here we take that distance to be of order Λ , the bilayer period. In the limit where the anisotropy is weak compared with the exchange field H_{ex} , the long-range coherence length ξ can be approximated as

$$\xi \simeq \Lambda \left(\frac{H_{\rm ex}}{H_{\rm r}}\right)^{2/(4-d)}$$

where d is the dimensionality. In this model, the local order makes a random walk in ddirections, gradually losing coherence over the length $\xi_{\rm m}$. In this case, it occurs only in the growth direction, so that d = 1, making $\xi_{\rm m} \propto H_{\rm ex}^{2/3}$. If $H_{\rm ex}$ varies as the inverse square of the non-magnetic layer thickness t as expected for RKKY coupling (Yafet 1987b), the model predicts $\xi_{\rm m} \propto t^{-4/3}$. If, on the other hand, $H_{\rm ex} \propto t^{-1/2}$, as suggested for transition metal systems (Mathon 1991), the coherence will decrease more gradually with layer thickness, $\xi_{\rm m} \propto t^{-2/3}$. These bracket the t^{-1} decrease that is observed. However, the model assumes that the local anisotropy direction is static and related to quenched-in disorder, whereas in reality the local anisotropy is developed within each layer during the ordering process. More complete models for the ordering process in rare-earth superlattices are not yet available, and this remains an area for future research.

6. Conclusions

The understanding of rare-earth metal nanostructures has advanced significantly over the decade since the first materials were grown. There can be no doubt that the present state of development remains rudimentary, however, and that a number of the most fundamental questions still remain unanswered. In writing this review we have nevertheless been aware that the general context and relative interest of the field for future research has become more clearly defined over the intervening years. It is therefore fair to ask whether the research field remains vital relative to contemporary alternatives. The following concluding comments attempt to address these questions.

It is undoubtedly true that the present capability for synthesizing new magnetic nanostructures from the rare-earth metals greatly exceeds the limited range of materials explored to date. In assessing the future opportunities we note that entire areas of compelling interest are eliminated by the constrained selection of materials in current use. Almost all completed studies have employed *c*-axis materials grown from a few selected metals, specifically Gd, Dy, Er and Ho, mainly with Y or Lu, and occasionally each other. Of these restrictions in scope, the limitation to (0001) growth perhaps constrains conceptual advances the most. Only a single investigation has explored magnetic properties of nanostructures grown along the *a* or *b* axes, and this with a view to fundamental matters of the induced exchange between spins. This remains the case despite the accessibility of growth procedures starting from sapphire for the controlled growth of $(1\bar{1}00)$, $(11\bar{2}0)$ and $(1\bar{1}02)$ materials, the latter at least with tunable vicinal

tilts (see sect. 3.4). As an example note that for any crystal orientation other than *c*-axis growth, magnetostriction in the helical phases is no longer fully constrained *locally*. Instead the magnetic state must be dressed in frozen phonons that describe the oscillatory state of strain, as indeed must also be the case for ferromagnetic states of superlattices grown in these orientations, and to relative degrees that offer a probe of magnetostrictive behavior on the atomic length scale. A perceptive application of such ideas surely offers a broad latitude in the design and synthesis of novel ordered states that have previously been inaccessible.

Rare-earth nanostructures also serve as tools to study fundamental problems in the magnetism of materials in various restricted geometries. There remains the question as to the possibility of creating 2D magnetic nanostructures that conform to an idealized Hamiltonian for which the theory is tractable and interesting. Some distance has been covered in the study of thin layers that approach the 2D limit, and a number of investigations relate to the way magnetic coherence is established in rare-earth superlattices at their antiferromagnetic and ferromagnetic transitions, but the connection with the expectations of idealized theoretical models remains to be established. Given the robust and predictable character of their magnetic moments and their interactions, these lanthanide metal systems have much to offer in the area of 2D magnetic behavior. Much the same can be said for the interlayer coupling; the way in which antiferromagnetic coherence is established at the Néel temperature remains, as noted above, quite poorly understood at the time of writing.

These nanostructures also offer an attractive approach to several fundamental problems of epitaxy. Of particular interest is the interaction of epitaxial strain with magnetic behavior, including stress relaxation during growth, and the relaxation at chosen temperatures of magnetoelastic strains introduced and selected by means of a magnetic field. The study of fluctuation, domain and surface processes in clamped magnetostrictive phases, like the analogous processes in ferroelectrics, remain badly understood in the face of considerable technical and scientific interest in connection with potential applications to switching, transduction and manipulation.

It may be unnecessary to note in addition that attention to date has largely been confined just to the magnetic properties of a few heavy lanthanides in simple nanostructures. The remaining metals, including the light lanthanides, are at least of equal interest, and promise still less conventional properties owing, for example, to the thermal excitation of modified core configurations that may be expected with confidence when a single 4f subshell is only partly occupied. Striking behavior has begun to be reported also in the electronic properties of rare-earth nanostructures where magnetotransport, for example, has exhibited anomalies that point both to strong modifications of bandstructure and important geometrical effects on interfacial scattering processes. As yet only few, isolated facts are available to prompt further activity in these new directions.

With the investigation of so many phenomena scarcely begun it seems appropriate to conclude this review by reminding the reader briefly of those features of the field that are now well established.

First, the means are available for synthesis of rare-earth nanostructures in a variety of crystal orientations, and for a variety of materials choices, all with interfacial mixing restricted to very few monolayers. The available methods are adapted to the preparation of structures of order 1 µm thick and lateral dimensions of inches, and the crystal quality may be regarded as quite satisfactory for metals, at least in the sense that growth defects play a limited role in the phenomena of most interest.

Second, the results available so far serve to confirm the role of induced exchange through the conduction electrons as the primary interaction that determines the ordering characteristics of the lanthanide moments. This has been most clearly established for the Dy/Y system, for which the helical magnetic waves propagate through many layers of nanostructures and so afford a precise determination of the periodicity and range of the interaction along the c-axis. In this same system alone, the reduced interaction range in, rather than normal to, the basal plane, has been established by experiments on b- and c-axis samples.

Third, and finally, it has been established that the lanthanide magnetism is in general remarkably robust, and in particular is insensitive to the interfaces, even in crystals only a few atomic layers thick. A reservation of critical importance in this regard is the central role of the state of strain in the description of the magnetic behavior. Specifically it has been established for Dy that epitaxial strains $\sim \pm 2\%$ are sufficient to double the Curie temperature or completely suppress the ferromagnetic phase. The twin assets of robustness and strain sensitivity make these materials at one time both ideal systems with which to explore epitaxial effects, and attractive models with which new states of magnetic order may be designed and synthesized.

Acknowledgements

We are greatly indebted to numerous colleagues who have contributed to our understanding of the rare-earth metals and rare-earth nanostructures. These include Drs. R.W. Erwin, M.V. Klein, and J.J. Rhyne, and our past close co-researchers J. Borchers, R. Beach, R.-R. Du, B.A. Everitt, B. Park and F. Tsui. To the latter two we owe a special debt for permission to include researches which remain, as yet, published only in their theses at the University of Illinois at Urbana-Champaign. The bulk of our research in this area, which forms a substantial part of this review, was supported by grants from the National Science Foundation. Most of the synthesis detailed in sect. 3 was funded by the Department of Energy, as was a portion of the synchrotron radiation work from our laboratories. Thanks are owed to the Office of Naval Research for funding part of the recent work on thin-film magnetostrictive behavior, which is a central theme of the review.

Appendix: Self-energy and pair interactions in linear response

A common problem has two bodies simultaneously perturbing a linear medium. Examples are two neighboring charges in a dielectric continuum, two bowling balls on a mattress,

or two spins interacting through an electron liquid – the problem of interest here. The term linear has a specific meaning. If bodies 1 and 2 at r_1 and r_2 separately cause linear perturbations $x_1(r-r_1)$ and $x_2(r-r_2)$, then acting together they cause a perturbation

$$x(r) = x_1(r - r_1) + x_2(r - r_2)$$
(A1)

for all r_1 and r_2 . Here we are concerned with the self-energies E_1 and E_2 of interaction between the separate bodies and the linear medium, and the total energy E_t when the two bodies interact with the medium simultaneously. The interaction energy is then defined as

$$E_{12} = E_t - E_1 - E_2. \tag{A2}$$

Thus defined, the interaction energy is negative when the energy is lowered by the interaction.

The calculations that follow employ a model in which an electronic medium is disturbed by point charges q_1 and q_2 . Suppose that in response to a charge q at r=0 the disturbed medium produces a potential qv(r) proportional to q. Then the net electrostatic potential is

$$V' = \frac{q}{r} + qv(r) + V_0,$$
 (A3)

with V_0 the interior potential in the absence of perturbing charges. Because the energy of the medium itself must depend on the square of the disturbance we may write it $\frac{1}{2}\beta v^2(0)$, and the net energy *E* associated with the interaction between the charge and the material is

$$E = qv(0) + \frac{1}{2}\beta v^{2}(0) = \frac{1}{2}\beta \left[v(0) + \frac{q}{\beta}\right]^{2} - \frac{q^{2}}{2\beta}.$$
 (A4)

This shows that the system minimizes its energy with $v(0) = -q/\beta$ with a net energy relaxation of

$$E = -\frac{q^2}{2\beta} = \frac{1}{2}\beta v(0).$$
 (A5)

By differentiation the energy change when $q \rightarrow q + \delta q$ is

$$\delta E = -\frac{q\delta q}{\beta} = v(0)\,\delta q. \tag{A6}$$

The result is just the energy of the added charge δq in the existing potential v(0), because this relaxed state is an energy minimum.

We need to calculate the relaxation energy when q_1 and q_2 are placed at r_1 and r_2 . For convenience suppose first that fractions x of the charges are in place, and the system is relaxed with a net potential

$$V(r) = xq_1v(r - r_1) + xq_2v(r - r_2).$$
 (A7)

Because the relaxed system is at an energy minimum, the energy change dE, when added charges dxq_1 and dxq_2 are placed at r_1 and r_2 , is $V_1dxq_1 + V_2dxq_2$, with V_1 , V_2 the potentials at r_1 and r_2 due to *external* charges. Hence

$$dE = \left(q_1 \left[\frac{q_2}{a} + q_1 v(0) + q_2 v(a)\right] + q_2 \left[\frac{q_1}{a} + q_2 v(0) + q_1 v(a)\right]\right) x \, dx.$$
(A8)

with $a = |r_1 - r_2|$. By integrating from x = 0 to x = 1, the total relaxation energy for the full charges is now found as

$$E_{12} = \frac{1}{2}(q_1^2 + q_2^2)v(0) + q_1q_2\left(\frac{1}{a} + v(a)\right).$$
(A9)

Here the first term is the sum of the two self-energies (eq. A5), and the second term is the desired interaction energy:

$$E_{12} = q_1 q_2 \left(\frac{1}{a} + v(a)\right).$$
 (A10)

Note that the result is just the energy needed to place the second charge in the medium with the material frozen in its relaxed configuration about the first charge (or vice versa). It includes both the direct interaction and the material-mediated interaction.

This prescription is quite general in linear response and is readily adapted to other cases. In the case of a medium of dielectric constant ϵ , for example, the induced polarization gives $q_1q_2[\epsilon^{-1} - 1]/a$ and the interaction energy becomes $q_1q_2/\epsilon a$. When this is augmented by the response of charged diffusing species, the induced term becomes $q_1q_2[\epsilon^{-1}e^{-\kappa_D a} - 1]/a$ and the interaction energy is $q_1q_2e^{-\kappa_D a}/\epsilon a$ with κ_D^{-1} the Debye–Hückel screening radius. For charges in a simple electron liquid the required dielectric response is the Lindhart function (see below).

These considerations are readily extended to obtain the interaction when two *disjoint* distributed charges $\rho_1(r)$ and $\rho_2(r)$ interact. For linear response the energy (A10) is merely summed over all δ -function pairs to find

$$E_{12} = \int \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \left[|\mathbf{r}_2 - \mathbf{r}_1|^{-1} + v(|\mathbf{r}_2 - \mathbf{r}_1|) \right].$$
(A11)

In a system with *many* disjoint perturbations the excess of the energy over the sum of the separate self-energies is just the sum $\sum E_{ij}$ of pair terms like eq. (A11) over all pairs *ij*. This is how the sum over pairs enter expressions for the RKKY energy.

Our present interest is in the case of spins interacting through an electron liquid, for which the direct term is just the dipolar interaction. The material-mediated term depends on the interaction between the core spin S and the conduction electrons. It is usually assigned the model form

$$E = \int j_{\rm sf}^{(1)} \mathbf{s} \cdot \mathbf{S} \,\delta(\mathbf{r} - \mathbf{r}_1) \,\rho(\mathbf{r}_1) \,\mathrm{d}^3 \mathbf{r}_1, \tag{A12}$$

with s the conduction electron spin and $\rho(r)$ the electron density. Suppose that ρ is the uniform initial density of conduction states with s parallel to a core spin S_1 . From eq. (A12) the density disturbance is

$$\delta \rho_{\rm up}(r) = \frac{1}{2} j_{\rm sf}^{(1)} S_1 \rho \, u(r), \tag{A13}$$

in which u(r) is the disturbance for a perturbation of *unit* energy and the $\frac{1}{2}$ is |s|. The spin-down disturbance is the same but negative. From eqs. (A10), (A12) and (A13) the induced interaction with a second spin S_2 having interaction $j_{sf}^{(2)}$ at a, and including the contribution of both spin senses, is

$$E_{12} = \frac{1}{2} (\mathbf{S}_1 \cdot \mathbf{S}_2) j_{\rm sf}^{(1)} j_{\rm sf}^{(2)} \frac{\rho^2 u(r)}{\rho}.$$
 (A14)

This is the RKKY result. It depends only on the interaction strengths $S_i j_{sf}^{(1)} \rho$ at the two sites and the *fractional* density disturbance $u(r)/\rho$ per unit interaction energy, which is the same for the full electron liquid as for either subband. As mentioned above, this energy is supplemented by the direct term, which is just the dipolar interaction.

References

- Aharony, A., and E. Pytte, 1980, Phys. Rev. Lett. 45, 1583.
- Aharony, A., and E. Pytte, 1983, Phys. Rev. B 27, 58723.
- Bates, S., and R.A. Cowley, 1988, J. Phys. C 21, 4113.
- Beach, R.S., 1992, Ph.D. Dissertation (University of Illinois) unpublished.
- Beach, R.S., J.A. Borchers, M.B. Salamon, R.-R. Du and C.P. Flynn, 1990, J. Appl. Phys. 67, 5710.
- Beach, R.S., J.A. Borchers, A. Matheny, J.J. Rhyne, C.P. Flynn and M.B. Salamon, 1991, J. Appl. Phys. 69, 4535.
- Beach, R.S., J.A. Borchers, R.W. Erwin, C.P. Flynn, A. Matheny, J.J. Rhyne and M.B. Salamon, 1992, J.

Magn. & Magn. Mater. 104-107, 1915.

- Beach, R.S., J.A. Borchers, R.W. Erwin, C.P. Flynn, A. Matheny, J.J. Rhyne and M.B. Salamon, 1993a, Phys. Rev. Lett. 70, 3502.
- Beach, R.S., J.A. Borchers, R.W. Erwin, C.P. Flynn, A. Matheny, J.J. Rhyne and M.B. Salamon, 1993b, J. Appl. Phys. 73, 6901.
- Bohr, J., J.D. Axe, C.L. Chien, K.L. D'Amico, D. Gibbs, M. Hong, J. Jensen, J. Kwo, C.F. Majkrzak and D.E. Moncton, 1989, Physica B 159, 93.
- Borchers, J.A., 1990, Ph.D. Dissertation (University of Illinois) unpublished.
- Borchers, J.A., R.-R. Du, R.W. Erwin, C.P. Flynn, J.J. Rhyne, M.B. Salamon and S. Sinha, 1987, J. Appl. Phys. 61, 4049.

- Borchers, J.A., R.-R. Du, R.W. Erwin, C.P. Flynn and M.B. Salamon, 1988a, Superlatt. and Microstr. 4, 439.
- Borchers, J.A., R.-R. Du, R.W. Erwin, C.P. Flynn, J.J. Rhyne and M.B. Salamon, 1988b, J. Appl. Phys. 63, 3458.
- Borchers, J.A., R.-R. Du, R.W. Erwin, C.P. Flynn, J.J. Rhyne and M.B. Salamon, 1991, Phys. Rev. B 43, 3123.
- Bruno, P., and C. Chappert, 1991, Phys. Rev. Lett. 67, 1602.
- Cable, J.W., and E.O. Wollan, 1968, Phys. Rev. 165, 733.
- Camley, R.E., C.L. Chien, M. Hong and J. Kwo, 1990, Phys. Rev. Lett. 64, 2703.
- Caudron, R., H. Bouchiat, A.J. Brown, R. Chung, P. Monod and J.L. Tholence, 1990, Phys. Rev. B 42, 2325.
- Chang, L.L., L. Esaki, W.E. Howard and R. Ludeke, 1973, J. Vac. Sci. Tech. 10, 11.
- Chudnovsky, E.M., W.M. Saslow and R.A. Serota, 1986, Phys. Rev. B 33, 251.
- Cooper, B.R., 1972, in: Magnetic Properties of Rare-Earth Metals, ed. R.J. Elliott (Plenum, London) p. 33.
- Coqblin, B., 1977, The Electronic Structure of Rare-Earth Metals and Alloys (Academic Press, London).
- Cunningham, J.E., and C.P. Flynn, 1985, J. Phys. F 15, L221.
- Cunningham, J.E., J.A. Dura and C.P. Flynn, 1988, in: Metallic Multilayers and Epitaxy, eds M. Hong, D.U. Gubser and S.A. Wolf (The Metallurgical Society) p. 77.
- de Gennes, P.G., 1958, C. R. Acad. Sci. 247, 1836.
- Dodson, B.W., and J.Y. Tsao, 1987, Appl. Phys. Lett. 51, 1325.
- Du, R.-R., and C.P. Flynn, 1990, J. Phys.: Condens. Matter 2, 1338.
- Du, R.-R., and C.P. Flynn, 1991, Surf. Sci. Lett. 258, L703.
- Du, R.-R., C.P. Flynn and F. Tsui, 1988, Phys. Rev. B 38, 2941.
- Durbin, S.M., J.E. Cunningham, C.P. Flynn and M.E. Mochel, 1981, J. Phys. F 11, L223.
- Durbin, S.M., J.E. Cunningham and C.P. Flynn, 1982, J. Phys. F 12, L75.
- Elliott, R.J., ed., 1972, Magnetic Properties of Rare-Earth Metals (Plenum, London).
- Elliott, R.J., and F.A. Wedgwood, 1964, Proc. Phys. Soc. London 84, 63.

- Erwin, R.W., J.A. Borchers, R.-R. Du, C.P. Flynn, J.J. Rhyne, M.B. Salamon and S. Sinha, 1987, Phys. Rev. B 35, 6808.
- Erwin, R.W., J.A. Borchers, R.-R. Du, J.J. Rhyne and M.B. Salamon, 1988a, J. Appl. Phys. 63, 3461.
- Erwin, R.W., J.A. Borchers, R.-R. Du, C.P. Flynn, J.J. Rhyne and M.B. Salamon, 1988b, J. Phys. (Paris) Colloq. 49, C8-1631.
- Erwin, R.W., J.J. Rhyne, J.A. Borchers, R.-R. Du, M.B. Salamon and C.P. Flynn, 1989, Physica B 161, 260.
- Erwin, R.W., J.A. Borchers, R.-R. Du, C.P. Flynn, J.J. Rhyne and M.B. Salamon, 1990, Mater. Res. Soc. Symp. Proc. 166, 133.
- Evenson, W.E., and S.H. Liu, 1968, Phys. Rev. 178, 783.
- Everitt, B.A., J.A. Borchers, R.W. Erwin, C.P. Flynn, B.J. Park, M.B. Salamon and F. Tsui, 1994, J. Appl. Phys. 75, 6592.
- Everitt, B.A., J.A. Borchers, R.W. Erwin, C.P. Flynn, B.J. Park, J.J. Rhyne and M.B. Salamon, 1995, J. Magn. & Magn. Mater. 140–144, 769.
- Fahrle, M., and W.A. Lewis, 1994, J. Appl. Phys. 75, 5604.
- Falicov, L.M., S.D. Bader, R. Gronsky, K.B. Hathaway, H.J. Hopster, D.N. Lambeth, S.S.P. Parkin, D.T. Pierce, G. Prinz, M.B. Salamon, I.K. Schuller and R.H. Victora, 1990, J. Mater. Res. 5, 1299.
- Farrow, R.F.C., B.D. Hermsmeier, S.S.P. Parkin, M.F. Toney and D.G. Wiesler, 1991, J. Appl. Phys. 70, 4465.
- Flynn, C.P., 1988, J. Phys. F 18, L195.
- Flynn, C.P., 1991, MRS Bulletin XVI, 30.
- Flynn, C.P., and S. Yadavalli, 1992, Acta Metal. Mater. 40, S45–52.
- Flynn, C.P., J.A. Borchers, J.E. Cunningham, R.T. Demers, R.-R. Du, J.A. Dura, R.W. Erwin, S.H. Kong, M.V. Klein, J.J. Rhyne, M.B. Salamon, F. Tsui, S. Yadaralli, H. Zabel and X. Zhu, 1989a, Proc. MRS Int. Conf. on Advanced Materials 10, 275.
- Flynn, C.P., R.W. Erwin, J.J. Rhyne, M.B. Salamon and F. Tsui, 1989b, J. Phys.: Condens. Matter 1, 5997.
- Freeman, A.J., 1972, in: Magnetic Properties of Rare-Earth Metals, ed. R.J. Elliott (Plenum, London) p. 281ff.
- Freund, L.B., 1993, in: Advances in Applied Mechanics, Vol. 30, eds J.W. Hutchinson and T.Y. Wu (Academic Press, New York) p. 1.
- Gibbs, D., J. Bohr, K.L. D'Amico, B.H. Grier and D.E. Moncton, 1985, Phys. Rev. Lett. 55, 234.

- Gibbs, D., J.D. Axe, J.A. Borchers, K.L. D'Amico and D.E. Moncton, 1986, Phys. Rev. B 34, 8182.
- Gibbs, D., D.R. Harshman, E.D. Isaacs, D.B. McWhan, D. Mills and C. Vettier, 1988, Phys. Rev. Lett. 61, 1241.
- Gibbs, D., M.B. Brodsky, G. Grübel, D.R. Harshman, E.D. Isaacs and H. Sowers, 1991, Phys. Rev. B 43, 5663.
- Goldschmidt, Y.Y., and A. Aharony, 1985, Phys. Rev. B 32, 264.
- Grünberg, P., M.B. Brodsky, Y. Pang, R. Schreiber and H. Sowers, 1986, Phys. Rev. Lett. 57, 2442.
- Herman, F., J. Sticht and M. van Schilfgaarde, 1992, Int. J. Mod. Phys. 7, 425.
- Huang, J.-C., R.-R. Du and C.P. Flynn, 1991a, Phys. Rev. Lett 66, 341.
- Huang, J.-C., R.-R. Du and C.P. Flynn, 1991b, Phys. Rev. B 44, 4060.
- Isaacs, E.D., D. Gibbs, J.B. Hastings, D.B. McWhan and D.P. Siddons, 1989, Phys. Rev. B 40, 9336.
- Jehan, D.A., K.N. Clausen, R.A. Cowley, N. Hagmann, D.F. McMorrow, R.C.C. Ward and M.R. Wells, 1993, Phys. Rev. B 48, 5594.
- Jensen, J., and A.R. Mackintosh, 1991, Rare Earth Magnetism (Clarendon Press, Oxford).
- Kasuya, T., 1966, in: Magnetism, Vol. VIIB, eds G.T. Rado and H. Suhl (Academic Press, New York) Ch. 3.
- Koehler, W.C., 1972, in: Magnetic Properties of Rare-Earth Metals, ed. R.J. Elliott (Plenum, London) Ch. 3.
- Kosterlitz, J.M., and D.J. Thouless, 1973, J. Phys. C 6, 1181.
- Kwo, J., J.E. Bower, F.J. Di Salvo, E.M. Gyorgy, M. Hong, D.B. McWhan and C. Vettier, 1985a, Phys. Rev. Lett. 55, 1402.
- Kwo, J., J.E. Cunningham, L.C. Feldman, E.M. Gyorgy, M. Hong and D.B. McWhan, 1985b, in: Layered Structure, Epitaxy and Interfaces, eds L.R. Dawson and J.H. Gibson (Materials Research Society, Pittsburgh, 1985) p. 509.
- Kwo, J., F.J. Di Salvo, M. Hong, C.F. Majkrzak and J.V. Waszczak, 1987, Phys. Rev. B 35, 7295.
- Kwo, J., J. Bohr, P. Böni, J.W. Cable, C.L. Chien, F.J. Di Salvo, R.M. Fleming, D. Gibbs, A.I. Goldman, H. Grimm, M. Hong, C.F. Majkrzak, D.B. McWhan, J.V. Waszczak and Y. Yafet, 1988, J. Phys. Colloq. 49, C8-1651.
- Kwo, R.J., 1987, in: Thin Film Growth Techniques for Low Dimensional Structures, eds R.F.C. Farrow,

A. Arrott, P.J. Dobson, J.H. Neave and S.P. Parkin (Plenum Press, London) p. 337.

- Li, D.Q., P.A. Dowben, K. Garrison and J. Zhang, 1993, J. Phys.: Condens. Matter 5, L73.
- Liu, S.H., R.P. Gupta and S.K. Sinha, 1971, Phys. Rev. B 4, 1100.
- Luche, M.C., A. Baudry and P. Boyer, 1993, J. Magn. & Magn. Mater. 121, 148.
- Majkrzak, C.F., J.W. Cable, M. Hong, J. Kwo, D.B. McWhan, C. Vettier, J.V. Waszczak and Y. Yafet, 1986, Phys. Rev. Lett. 56, 2700.
- Majkrzak, C.F., J. Bohr, P. Böni, J.W. Cable, C.L. Chien, R.M. Fleming, C.P. Flynn, D. Gibbs, A.I. Goldman, H. Grimm, M. Hong, T.C. Hsieh, J. Kwo, A. Matheny, D.B. McWhan and Y. Yafet, 1988, J. Appl. Phys. 63, 3447.
- Majkrzak, C.F., J. Bohr, C.L. Chien, D. Gibbs, M. Hong, J. Kwo and Y. Yafet, 1991, Adv. Phys. 40, 99.
- Massalski, T.B., 1986, Binary Alloy Phase Diagrams (ASM, Metals Park, OH).
- Mathon, J., 1991, Contemp. Phys. 32, 143.
- Matthews, J.W., 1979, in: Dislocations in Solids, Vol. 2, ed. F.R.N. Nabarro (North-Holland, Amsterdam) p. 461.
- Mayer, J., J.A. Dura, C.P. Flynn, G. Gutenkundst, G. Mobus and M. Ruhle, 1992, Acta Metall. Mater. 40, S217–225.
- McMorrow, D.F., R.A. Cowley, D.A. Jehan, P.P. Swaddling, R.C.C. Ward and M.R. Wells, 1993, Physica B 192, 150.
- McWhan, D.B., 1985, in: Layered Structures and Epitaxy, eds L.R. Dawson and J.M. Gibson, MRS Symp. Proc. **37**, 493.
- Park, B., 1994, Thesis (University of Illinois) unpublished.
- Parkin, S.S.P., 1991, Phys. Rev. Lett. 67, 3598.
- Reimer, P.M., J.A. Dura, C.P. Flynn and H. Zabeł, 1992, Phys. Rev. B 45, 11426.
- Reimer, P.M., S. Blasser, C.P. Flynn, A. Matheny, K. Ritley, J.J.M. Steiger, A. Weidinger and H. Zabel, 1993, Z. Phys. Chem. 181, 367.
- Rhyne, J.J., 1972, in: Magnetic Properties of Rare-Earth Metals, ed. R.J. Elliott (Plenum, London) Ch. 4.
- Rhyne, J.J., J.A. Borchers, R.-R. Du, R.W. Erwin, C.P. Flynn, M.B. Salamon and S. Sinha, 1987, J. Appl. Phys. 61, 4043.
- Rhyne, J.J., J.A. Borchers, R.-R. Du, R.W. Erwin, C.P. Flynn and M.B. Salamon, 1988, Phys. Scripta T 29, 31.

- Rhyne, J.J., J.A. Borchers, R.-R. Du, R.W. Erwin, C.P. Flynn and M.B. Salamon, 1989, J. Less-Common Met. 148, 17.
- Rosen, M., D. Kalir and H. Klimker, 1973, Phys. Rev. B 8, 4399.
- Salamon, M.B., and D.S. Simons, 1973, Phys. Rev. B 7, 229.
- Salamon, M.B., A. Borchers, J.E. Cunningham, R.W. Erwin, C.P. Flynn, J.J. Rhyne and S. Sinha, 1986, Phys. Rev. Lett. 56, 259.
- Salamon, M.B., R.S. Beach, J.A. Borchers, R.-R. Du, R.W. Erwin, C.P. Flynn, J.J. Rhyne and F. Tsui, 1991, Phys. Scripta T 35, 163.
- Salamon, M.B., R.S. Beach, J.A. Borchers, R.W. Erwin, C.P. Flynn, A. Matheny, J.J. Rhyne and F. Tsui, 1992a, J. Magn. & Magn. Mater. 104–107, 1729.
- Salamon, M.B., R.S. Beach, J.A. Borchers, R.W. Erwin, C.P. Flynn, A. Matheny, J.J. Rhyne and F. Tsui, 1992b, Mater. Res. Symp. Proc. 231, 95.
- Schuller, I.K., 1980, Phys. Rev. Lett. 44, 1597.
- Simpson, J.A., K.N. Clausen, R.A. Cowley, D.A. Jehan, D.F. McMorrow, R.C.C. Ward and M.R. Wells, 1994, Phys. Rev. Lett. 73, 1162.
- Squires, G.L., 1978, Introduction to the Theory of Thermal Neutron Scattering (Cambridge University Press, Cambridge) ch. 7.
- Stanley, H.E., 1971, Introduction to Phase Transitions and Critical Phenomena (Oxford University Press).
- Steiger, J.J.M., L.J. de Jongh, E. Frikkee and W.J. Huiskamp, 1983, Physica B 120, 202.
- Tanaka, Y., J.A. Borchers, R.-R. Du, C.P. Flynn, D. Gibbs, G. Helgeson, P. Wochner and M.B. Salamon, 1995, Jpn. Phys. Soc., abstract, to be published.

- Tsui, F., 1992, Ph.D. Dissertation (University of Illinois) unpublished.
- Tsui, F., and C.P. Flynn, 1993, Phys. Rev. Lett. 71, 1462.
- Tsui, F., and C.P. Flynn, 1995, to be published.
- Tsui, F., J.A. Borchers, R.W. Erwin, C.P. Flynn, J.J. Rhyne and M.B. Salamon, 1991, Phys. Rev. B 43, 13320.
- Tsui, F., J.A. Borchers, R.W. Erwin, C.P. Flynn, J.J. Rhyne and M.B. Salamon, 1992, J. Magn. & Magn. Mater. 104–107, 1901.
- Tsui, F., R.S. Beach, J.A. Borchers, R.W. Erwin, C.P. Flynn and J.J. Rhyne, 1993a, J. Appl. Phys. 73, 6904.
- Tsui, F., C.P. Flynn and D. Han, 1993b, Phys. Rev. B 47, 13648.
- Tsui, F., C.P. Flynn and B.J. Park, 1995, Phys. Rev. Lett., submitted.
- Van der Merwe, J.H., 1950, Proc. Phys. Soc. London Sect. A 63, 616.
- Van der Merwe, J.H., 1962, Philos. Mag. 7, 1433.
- Vettier, C., B.W. Batterman, B.M. Buntschuh, E.M. Gyorgy and D.B. McWhan, 1986, Phys. Rev. Lett. 56, 747.
- Xia, J.-B., and Y.-C. Chang, 1992, Phys. Rev. B 46, 10894.
- Yafet, Y., 1987a, J. Appl. Phys. 61, 4058.
- Yafet, Y., 1987b, Phys. Rev. B 36, 3948.
- Yafet, Y., M. Hong, J. Kwo, C.F. Majkrzak and T. O'Brien, 1988, J. Appl. Phys. 63, 3453.
- Yang, M.-H., and C.P. Flynn, 1989, Phys. Rev. Lett. 62, 2476–2479.
- Yang, M.-H., and C.P. Flynn, 1995, in preparation.
- Zhou, G., 1995, private communication.

Chapter 148

NANOSCALE RARE EARTH-TRANSITION METAL MULTILAYERS: MAGNETIC STRUCTURE AND PROPERTIES

Z.S. SHAN and D.J. SELLMYER

Behlen Laboratory of Physics and Center for Materials Research and Analysis, University of Nebraska, Lincoln, NE 68588-0113, USA

Contents

	List	of syn	ibols		82	
1.	Introduction					
2.	Magnetic structure				86	
	2.1.	Magn	etic strue	cture and interfacial		
		magnetism				
	2.2. Magnetic interactions in R and R-T					
		alloys			87	
3.	Exp	erimen	tal prope	rties of R/T multilayers	89	
	3.1. Layered structure				89	
	3.2. Magnetic properties of Dy/Fe, Dy/Co					
		and T	b/Fe		91	
		3.2.1.	Dy/Fe		91	
			3.2.1.1.	Layer-thickness		
				dependence of		
				magnetic properties at		
				room temperature	91	
			3.2.1.2.	Temperature dependence		
				of magnetic properties	94	
		3.2.2.	Dy/Co		95	
			3.2.2.1.	Layer-thickness		
				dependence of		
				magnetic properties at		
				room temperature	95	
			3.2.2.2.	Temperature dependence		
			/_	of magnetic properties	99	
		3.2.3.	Tb/Fe		100	
			3.2.3.1.	Layer-thickness		
				aependence of		
				magnetic properties at	101	
				room temperature	101	

		3.2.3.2. Temperature dependence	
		of magnetic properties	101
		3.2.4. Interface anisotropy	105
	3.3.	Mössbauer measurements	108
		3.3.1. Tb/Fe	109
		3.3.1.1. Orientation of Fe	
		moment	109
		3.3.1.2. Interfacial magnetism	110
		3.3.2. Dy/Fe and Nd/Fe	113
	3.4.	Magnetic circular X-ray dichroism	
		measurements	113
4.	The	oretical model for magnetization and	
	anis	otropy	116
	4.1.	Magnetization distribution	116
	4.2.	Perpendicular magnetic anisotropy	
		(PMA)	119
		4.2.1. The origin of PMA in R/T	119
		4.2.2. PMA model for R/T	121
		4.2.3. Analysis for Dy/Co and Tb/Fe	124
		4.2.4. PMA for Gd/T (T = Co, Fe)	125
		4.2.5. Magnetic anisotropy for Dy/M	
		(M = Ta, Cu and Y)	125
5.	Mag	netization reversal and microscopic	
	effe	cts	125
	5.1.	Magnetization reversal	125
		5.1.1. Tb/Fe	126
		5.1.2. Dy/Fe	128
		5.1.3. Magnetization reversal model	130
		5.1.4. Micromagnetic calculations	132
	5.2.	Demagnetization anisotropy in CMF	133

5.3. Measurements of anisotropy and the		6. Summary and conclusion	139
R-T exchange coupling	134	Acknowledgments	140
5.4. Orientation of magnetic moments in		References	140
CMF	136		

List of symbols

A_{j0}	average atomic concentration of <i>j</i> th	J_0	average ferromagnetic exchange
	constituent ($j = 1$ and 2 refer to T and R	ΔJ_{ij}	exchange fluctuation
A_{j}	constituents, respectively) modulation amplitude of the <i>j</i> th	J_{Z}	Z component of R subnetwork angular momentum
	constituent concentration $(j=1 \text{ and } 2$ refer to T and R constituents,	$J_{\mathrm{R-T}}$	exchange constant between R and T subnetworks
40	respectively)	Ku	intrinsic anisotropy
A_2°	ions	K'_{u}	measured anisotropy including the demagnetization anisotropy
BOA	bond-orientational anisotropy	Ki	interface anisotropy
CMF	compositionally modulated film	K _v	volume anisotropy
D'	crystal-field coefficient (Wang and	K _{de}	demagnetization anisotropy
D	Kleemann 1991)	K _{st}	stress anisotropy
D	average local unfaxial anisotropy in the Hamiltonian of R and R–T alloys	K(i)	intrinsic anisotropy of the <i>i</i> th slice of a multilayer
$d_{\mathrm{Tb}} (d_{\mathrm{Co}})$	Tb layer thickness (Co layer thickness)	k _B	Boltzmann constant
DCD	DC demagnetizing remanence	Ĺ	orbital angular momentum
F	magnetization	М	nonmagnetic metal, e.g. Cu, Ta, etc.
L_{W}	a measure of the wall energy associated with magnetization reversal	М	magnitude of magnetization M
	of small volume	M _s	saturation magnetization
EXAFS	extended X-ray absorption fine structure	M _R	R subnetwork magnetization
$g_{\rm R}$ $(g_{\rm T})$	gyromagnetic factor of R atom (T atom)	Μ _T	T subnetwork magnetization
H	applied magnetic field	MCXD	magnetic circular X-ray dichroism
H'	field in the film plane in the Tb/Fe multilayers produced by the Fe layers	Ν	atomic concentration or the number of atoms per unit volume
	(Wang and Kleemann 1991, 1992)	ĥ _i	local easy axes at i site
$H_{\rm c}$	coercivity	O_m^n	Stevens' operator
$H_{c\perp}$	coercivity measured as the applied field	PMA	perpendicular magnetic anisotropy
	is perpendicular to the film plane	R	lanthanide metal (e.g. Dy, Tb, etc.)
$H_{\rm DW}$	domain wall critical field in magnetization reversal	R	rate of domain nucleation in magnetization reversal
H_{N}	nucleation critical field in magnetization reversal	$R_{\rm j}(r)$	isotropic part of the distribution of constituent ions
$H_{\rm f}$	fluctuation field in magnetization reversal	$\langle r^2 \rangle$	average radius squared of the 4f electrons
\widehat{H}_{j}	local demagnetizing field at the <i>j</i> th cell in the magnetization reversal model	RMA S	random magnetic anisotropy
H_z	Z component of the applied field	<i>w</i> _i	R-T alloys
IRM	isothermal remanence magnetization	S(H)	magnetic viscosity at the applied field H

Т	transition metal (e.g. Fe, Co, etc.)	μ_i	magnetic moment at <i>i</i> site
Т	temperature (K)	μ^+ (μ^-)	absorption coefficient for an antiparallel
TEM	transmission electron microscopy		(parallel) orientation of photospin
UHV	ultra-high vacuum		relative to the magnetization direction in
V _c	assumed cell volume of magnetization reversal in the model proposed by Kirby et al. (1994)	$ ho_j$	charge density at j site or charge density of jth constituent ($j=1$ and 2 refer to T and R constituents respectively)
$V_{\rm w}$	domain wall velocity	σ	magnetization
υ	activation volume in magnetization	σ	saturation magnetization or spontaneous
	reversal	0 _s	magnetization
VSM	vibrating sample magnetometer	$\sigma_{\perp}(\sigma_{\parallel})$	magnetization measured as the applied field is perpendicular (parallel) to the
Ζ	Z axis along the film normal direction		
Ζ	coordination number of an ion		film plane
α _J	Stevens' factor	$\sigma_{C_0}(\sigma_{Dy})$	Co (Dy) subnetwork magnetization
$\beta_j(r)$	the lowest-order anisotropic distribution of <i>j</i> th constituent ions ($j=1$ and 2 refer to T and R constituents, respectively)	σ_j	magnetization of <i>j</i> th constituent $(j = 1$ and 2 refer to T and R constituents, respectively)
γ	initial radius of the domain in magnetization reversal	σ_z	Z component of R subnetwork magnetization
η_j	atomic concentration of <i>j</i> th constituents	τ	torque
(j=1 and 2 refer to T and R constituents, respectively)	(j=1 and 2 refer to T and R constituents, respectively)	$\chi_{\rm irr}(H)$	irreversible susceptibility measured at the applied field H
Λ	coupling strength between R and T subnetworks	$\chi^{i}_{irr}(H)$	differential of the isothermal remanence curve (IRM)
٨	mean-field coupling coefficient	$\gamma^{d}(H)$	differential of the DC demagnetizing
λ	bilayer thickness of the multilayers	vm()	remanence curve (DCD)
$\mu_{ m B}$	Bohr magneton		

1. Introduction

The goal of this chapter is to review recent advances in our understanding of the magnetic structure, the interfacial magnetism, and the origin of perpendicular magnetic anisotropy (PMA) of lanthanide-transition metal nanoscale multilayers, here denoted as R/T. We do not intend to review all of the recent work on these subjects, but rather will focus on discussing either newly understood phenomena by means of a few illustrative experiments, or those aspects which are not yet understood and therefore require additional work.

In recent years, lanthanide-transition metal nanoscale multilayers have been the subject of great interest and their properties have been studied intensively. The reasons for this include pure physics of interfacial magnetism and low-dimensional effects and also their promising magnetic properties with possible applications for perpendicularmagnetic and magneto-optical recording. Physically, such attractive properties come from the controlled local atomic environments in the artificially layered structure. Modern deposition systems increasingly have been used to produce multilayers with controlled





local atomic environments and microstructure which lead to physically interesting and technologically useful properties. Much of the driving force for this research has come from the hope that, with enough understanding and control of the microstructure and its relationship to properties, it will become easy to design the recording media for data storage or to create hard or semihard film magnets which can be coupled with semiconducting integrated circuits, micromachines, microsensors, etc.

The multilayers discussed in this chapter were prepared by sputtering systems or thermal evaporation in UHV, but mainly by using multiple-gun sputtering, such as shown schematically in fig. 1. There are many controllable parameters available in a sputtering system (e.g. sputtering pressure, rate, power, time, substrate temperature, etc.) to affect or adjust the local atomic arrangements and a variety of multilayered structures can be grown as illustrated in fig. 2. Figure 2a exhibits a coherent layered structure or, equivalently, a single-crystal superlattice. A compositionally modulated alloy with disorder at the interfaces is shown schematically in fig. 2b. Increasingly complex models of crystalline, amorphous and mixed nonmagnetic and magnetic multilayers are shown in figs. 2c–f. Particularly by employing either a light or a heavy lanthanide in combination with a transition metal, it is possible to construct the ferromagnetic or ferrimagnetic structures shown in figs. 2e and f which will be discussed often in the course of this chapter.



Fig. 2. Schematic examples of various types of multilayers or compositionally modulated films (CMF).

In R/T multilayers, the PMA, which is produced by the interaction between 4f electrons of R ions and the electric gradient field of the neighbor ions, is at the heart of the interfacial magnetism. An additional desirable feature of the lanthanides is that their chemical similarity leads to easy substitution of one for another. Furthermore, their Hund's rule interaction and the presence or absence of orbital angular momentum produces a wide range of ferromagnetic or ferrimagnetic structures when combined with T ions, and either very strong or rather weak magnetic anisotropies. It is seen that the interactions among all the R and T atoms is the basis for understanding the magnetic interactions and structures that are important for understanding amorphous R and R–T alloys. The roles that random magnetic anisotropy and exchange interactions play in determining the magnetic structure will be emphasized.

For the multilayered structure there are many interfaces, each of which is characterized by reduced symmetry in the surrounding atoms, and this feature favors PMA as was first pointed out by Néel (1954). Therefore one may expect that the multilayered structure may exhibit more anisotropic magnetic properties compared with the homogeneous films. However, this advantage of multilayers, i.e. the abundance of interfaces, also introduces complications in understanding the magnetic properties analytically because of the inhomogeneous atomic arrangements in the interface region. In sect. 3, the experimental results of R/T multilayers (R=Tb, Dy; T=Fe, Co) are summarized briefly. The roles of interfacial magnetism in determining the effects of the layer thickness and temperature-dependent magnetic properties are emphasized. Based on the abundant results of experiments, a detailed physical model, which shows clearly the origin of PMA and gives the possibility to determine the magnetization distribution, will be introduced in sect. 4.

In sect. 5 the magnetization reversal, which is an interesting topic in physics and an important aspect of very high density recording media, and some microscopic effects, such as the R-T exchange coupling effects on the anisotropy near the compensation point, will be discussed. Finally, we conclude with a summary and give some suggestions for future work on unsolved problems.

2. Magnetic structure

2.1. Magnetic structure and interfacial magnetism

The magnetic structure of artificially deposited multilayers containing heavy R, which couples antiferromagnetically with T in the interface region, is shown schematically in fig. 3. In fig. 3a, which represents relatively thicker layers (say >50 Å), the R will be disordered at room temperature, the T (e.g. Fe) will be ordered ferromagnetically and there will be an interface region with scattered R moments because of the disordered structure and random magnetic anisotropy. In the interior T region, the magnetic moment is usually parallel to the film plane. Thus multilayers with thick individual layer thicknesses will show a two-phase characteristic of R and T because the interface contribution is negligibly small. In the case of thinner individual layers (say 5–10 Å) as shown in fig. 3b, because of the mixing between R and T layers the X-ray diffraction data indicate an amorphous structure with sinusoidal compositional modulation (fig. 3c). The interfaces may give the major contribution to the magnetic moments as the nominal layer thicknesses of R and T decrease until the interface dominates and then the net magnetic moment may be perpendicular to the film plane.

The rest of this chapter will be focused on R/T multilayers with thin layers where the interfacial magnetism plays a major role. Many of the outstanding properties, such as large PMA, controlled coercivity and compensation point in multilayers, are associated with the interfacial magnetism. The temperature dependence of magnetic properties is controlled by the interfacial magnetism, which also is the key to obtain the desired properties for practical applications.

The interfaces may be regarded as compositionally modulated disordered R-T alloys because X-ray diffraction shows an amorphous structure in the interface region. In the next subsection a brief overview of the interactions and structures of R and R-T alloys is given, on the basis of which the magnetic structure of interfaces and the origin of PMA may be well understood.



Fig. 3. Schematic diagrams of magnetic structure for (a) thick (Int. = interface regions) and (b) thin R/T multilayers; (c) compositional modulation for the thin case (after Shan and Sellmyer 1990b).

2.2. Magnetic interactions in R and R-T alloys

In an amorphous R material it is important to account for the possibility of fluctuation and randomness in both exchange interactions and directions of local single-ion anisotropy and this leads to the Hamiltonian (Sellmyer and Nafis 1985)

$$H = -\sum_{ij} (J_0 + \Delta J_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j - \mathbf{D} \sum_i (\hat{\mathbf{n}}_i \cdot \mathbf{S}_i)^2,$$
(1)

in which the first term represents the exchange and the second term the random magnetic anisotropy (RMA). The local easy axes (\hat{n}_i) are taken as random from site to site. S_i (S_j) is the atomic spin at *i* site (*j* site), J_0 is an average ferromagnetic exchange, ΔJ_{ij} represents the exchange fluctuations, and *D* an average local uniaxial anisotropy arising from electric field gradients of neighboring atoms. If ΔJ_{ij} are taken to be zero, eq. (1) becomes the Harris–Plischke–Zuckermann Hamiltonian in which the effect of the first term is to align the spins (if $J_0 > 0$) while the RMA term tends to scatter them. Figure 4 presents a schematic phase diagram in which $t=k_{\rm B}T/J_0$, $\alpha=D/J_0$ and $\delta=\langle \Delta J \rangle/J_0$. Clearly in the $\alpha=0$ plane one has the possibility for ferromagnetism (F) for small δ values, a spin-glass-like phase (SG) for large δ values and there also is the possibility of a mixed phase (M) in the intermediate region. On the other hand in the $\delta=0$ case a speromagnetic (spin scattered) structure (SM) exists for large α values



Fig. 4. Schematic phase diagram of possible magnetic states in the presence of RMA and exchange fluctuations (after Sellmyer and Nafis 1985). See the text for the identification of the various symbols and acronyms. MCP = multi-critical point.

and a correlated speromagnetic structure (CSM) exists for small α values where there is short-range ferromagnetic order. It can be seen that in the presence of all three terms in the Hamiltonian there will be a complicated three-dimensional phase to be considered.

Figure 5 shows some examples discussed above in which there are speromagnetic, asperomagnetic and ferrimagnetic structures depending on the presence of RMA in the first two cases and its absence in the third case. When there are both lanthanide and transition metals such as Fe and Co present, i.e. R–T disordered alloys, one can obtain even more complex structures as illustrated in the lower part of fig. 5. An important point is that the heavy lanthanide moments tend to couple antiparallel whereas the light lanthanides couple parallel to the T moments.

On the basis of the above consideration the magnetic structure of heavy R-T alloys in the interface region may have sperimagnetic features with random orientation of the local easy axes. For the material to show a macroscopic anisotropy, there must be an orientational coherence to these local anisotropy axes. The interfaces in R/T multilayers may have such desired structure to offer this orientational coherence. In sect. 3, the experimental evidence is presented and in sect. 4 a detailed model, which clearly shows such orientational coherence, is discussed.



Fig. 5. Schematic diagram and definitions of phases possible in one- and twocomponent RMA systems (after Sellmyer and O'Shea 1983).

3. Experimental properties of R/T multilayers

In this section we give a brief review of the experimental results including the layered or compositionally modulated structure for R/T multilayers, the layer thickness and temperature dependencies of magnetic properties for Dy/Fe, Dy/Co and Tb/Fe multilayers. We will not provide a comprehensive review of all recent work in this field. Rather, our aim is to focus on discussing the above fundamental properties, and only limited references which are closely related to this discussion are cited. The role that the interfacial magnetism plays in determining magnetic properties will be emphasized.

Mössbauer measurements, which are used to determine the local Fe moment and its direction at different temperatures for Tb/Fe, Dy/Fe and Nd/Fe, are presented in this section. Magnetic circular X-ray dichroism (MCXD) is a relatively new element-selective technique, which can be used to obtain information on magnetic properties for both R and T atoms; one example of MCXD studies of Tb/Fe multilayers is given.

3.1. Layered structure

The layered structure of R/T multilayers can be investigated by X-ray diffraction and transmission electron microscopy (TEM). One example of small angle X-ray diffraction for 3.7 Å Tb/2.5 Å Fe and 16 Å Tb/30 Å Fe multilayers prepared by Sato (1986) is shown in figs. 6a and b with only first and up to fourth order of diffraction peaks, respectively. Two TEM micrographs for 4.8 Å Tb/10.5 Å Fe and 16 Å Tb/30 Å Fe are shown in fig. 7 and the periodic distributions of Tb and Fe are observed (Sato 1986). A brief summary of the small-angle X-ray diffraction peaks for R/T (R=Tb, Dy, Nd; T=Fe, Co, Ni) is listed in Table 1.



Fig. 6. The small-angle X-ray diffraction patterns for (a) 3.7 Å Tb/2.5 Å Fe and (b) 16 Å Tb/30 Å Fe (after Sato 1986).



Fig. 7. Transmission electron micrographs of the cross-section for (a) 4.8 Å Tb/10.5 Å Fe and (b) 16 Å Tb/30 Å Fe (after Sato 1986).

It is concluded from table 1 that for most of the samples only the first diffraction peak, which implies sinusoidal composition modulation, is observed for the bilayer thicknesses $\lambda < 30$ Å. This implies that R/T multilayers with thin layers have diffuse interfaces and

the individual layer thickness					
R/T	1st Peak	2nd Peak	3rd Peak	4th Peak	Ref.
Tb/Fe	3.7Å Tb/2.5Å Fe	<u></u>		16Å Tb/30Å Fe	1
Tb/Fe	λ≤12 Å				2
Tb/Fe	λ≤15Å				3
Tb/FeCo	$\lambda = 21 \text{ Å}$	$\lambda = 31.5 \text{ Å}$			4
Tb/Co	$d_{\mathrm{Tb}}, d_{\mathrm{Co}} \ge 15 \mathrm{\AA}$		30Å Tb/30Å Co		5
ТЬ/Со		$\lambda = 37 \text{ Å}$	$\lambda = 72 \text{ Å}$		6
Dy/Fe ^a					7
Dy/Fe	λ≥10 Å				8
Dy/Fe	14Å Dy/40Å Fe				9
Nd/Fe	λ≥10Å				10

Table 1 A summary of the small X-ray diffraction peaks for various R/T multilayers. λ is bilayer thickness and d is the individual layer thickness

 a No peaks were observed for ~3Å Dy/11–22Å Fe and 17Å Dy/~2Å Fe.

References

(6) Honda et al. (1987)
(7) Yoden et al. (1988)
(8) Sato and Habu (1987)
(9) Shan and Sellmyer (1990b)
(10) Mibu et al. (1989)



Fig. 8. Small-angle X-ray diffraction patterns for 4.8 Å Tb/10.5 Å Fe: (a) as deposited; (b) after annealing at 250°C for 5 hours (after Sato 1986).

these are sometimes called compositionally modulated films (CMF) instead of multilayers. We notice that R/T CMFs have much more diffuse interfaces compared with the Co/Pt, Pd and Au multilayers which usually show 3rd-4th order peaks (Shan et al. 1994) and up to the 7th order peak for Co/Au multilayer (Zhang et al. 1993).

An example of the annealing effect on the small angle X-ray diffraction peak of 4.8 Å Tb/10.5 Å Fe before and after annealing at 250°C for 5 hours is illustrated in fig. 8a and b. The peak intensity decreases because of the intermixing between Tb and Fe atoms at the interface boundaries; however, the layered structure still exists.

3.2. Magnetic properties of Dy/Fe, Dy/Co and Tb/Fe

3.2.1. Dy/Fe

3.2.1.1. Layer-thickness dependence of magnetic properties at room temperature. Figure 9a (Shan and Sellmyer 1990b) shows a detailed Fe layer-thickness dependence of hysteresis loops for 5 Å Dy/X Å Fe as the Fe layer thickness varies from 2.5 Å to 40 Å; note especially that the interval is only 1.25 Å as X ranges from 2.5 to 10 Å. The layer-thickness dependences of magnetization and anisotropy determined from fig. 9a are summarized in fig. 10.

Several results about the magnetization can be found from figs. 9a and 10. To understand the layer-thickness dependence of magnetization, both the antiferromagnetic coupling of Dy and Fe moments and the modulated distribution of composition have to be taken into account. (i) Sample 5 Å Dy/6.25 Å Fe is in a state close to the compensation point: the Dy moment dominates for X < 6.5 Å and the Fe moment dominates for X > 6.5 Å. (ii) As X increases from 2.5 to 6.5 Å, the magnetization magnitude of Dy/Fe, $|\sigma|$, first increases, then decreases. This feature is due to the existence of two competitive





Fig. 10. Fe layer-thickness dependence of magnetization and measured anisotropy for 5 Å Dy/X Å Fe at 300 K (after Shan and Sellmyer 1990b).

processes: the enhancement of the Dy moments by the exchange interactions between Fe and Dy subnetwork moments as the Fe atomic fraction increases in this range, and the antiferromagnetic coupling between the Dy and Fe subnetwork moments. The former dominates as X is close to 2.5 Å and the latter prevails as X approaches 6.5 Å. (iii) As X increases from 12 to 20 Å the magnetization of σ_{\parallel} and σ_{\perp} changes very little, where \parallel and \perp represent measurements parallel or perpendicular to the film plane. This may be attributed to the fact that the pure amorphous Fe is disordered magnetically; as the Fe layer thickness ranges between 10 Å and 20 Å, the Fe atomic fraction in the central region of the Fe layer is close to unity and its structure is amorphous which gives no contribution to the moments. Therefore the magnetization exhibits a "kink" there. Honda et al. (1991a) also reported such behavior in Fe/DyFe multilayers. They found that when the Fe layer thickness $d_{\rm Fe}$ decreases, the crystallographic structure of the Fe layer changes from bodycentered-cubic to amorphous at around 20 Å. At this critical thickness, the spontaneous magnetization and the Kerr rotation angle are nearly zero and the magnetization curve does not show hysteresis or saturation indicating its spin-glass-like or superparamagnetic nature. (iv) For X > 20 Å, the Fe has crystalline structure and its moment increases rapidly as shown in the figs. 9a and 10. (v) It is noticed that the four samples of 5 Å Dy/X Å Fe (X=2.5, 6.25, 15, 20) exhibit the character of smaller magnitude of magnetization and this can be interpreted as follows. Sample 5 Å Dy/2.5 Å Fe is just ordered weakly by the exchange interactions between Dy and Fe moments and has an almost homogeneous distribution of Fe and Dy constituents because both the Fe and Dy layers are very thin. Sample 5 Å Dy/6.25 Å Fe displays almost zero magnetization since the Dy moment dominates in the Dy region and the Fe moment dominates in the Fe region and they compensate each other to produce a nearly zero net magnetization. However, sample 5 Å Dy/15 Å Fe (or 5 Å Dy/20 Å Fe) has a much thicker Fe layer and the central Fe region gives no magnetization contribution as mentioned above. (vi) As the Dy layer becomes thicker (not shown in fig. 10) the compensation point will move toward larger Fe layer thickness and this is understandable from the antiferromagnetic coupling of Dy and Fe moments.

The layer-thickness dependence of the magnetic anisotropy, as shown in figs. 9a and 10, exhibits the following features. (i) Figure 9a shows that the hysteresis loops of σ_{\parallel} change their shapes very little as the Fe layer thickness varies from 5 to 20 Å, whereas the hysteresis loops of σ_{\perp} change their characteristics noticeably in the same range. When the Fe layer is thicker than 30 Å, the hysteresis loops of σ_{\parallel} also change noticeably. This implies that the magnetic properties in the direction perpendicular to the film plane strongly depend on the "interface" which is characterized by the anisotropic distribution of constituent atoms, but the magnetic properties in the parallel direction are mainly determined by the "inner part" of the Fe layer. (ii) The samples with the layer thickness thinner than about 12 Å usually have perpendicular anisotropy for both the 2.5 Å < X < 6.25 Å region where the Dy moment dominates and the 6.25 Å < X < 12 Å region where the Fe moment dominates. This suggests that the source of the perpendicular anisotropy is related to the anisotropic distribution and constituent magnetization rather than their net magnetization. (iii) The behavior of the uniaxial anisotropy, K_{u} , at the compensation point is uncertain. Sato and Habu (1987) reported that $K_u = 0$ at the compensation point for Dy/Fe, Tb/Fe, and Gd/Fe CMF. But in the case of nominally homogeneous R-T films van Dover et al. (1985) and Egami et al. (1987) claimed that $K_{\rm u}$ changes smoothly through the compensation point. This problem will be discussed in more detail in sect. 5.2.

Figure 9b (Shen 1994) shows the Dy layer-thickness dependence of hysteresis loops of Y Å Dy/5 Å Fe as the Dy layer thickness varies from 6.5 Å to 5 Å; note especially (i) although the thickness interval is only 0.5 Å, the coercivity and magnetization are very strongly dependent on thickness as the Dy layer thickness Y approaches 5 Å where sample 5 Å Dy/5 Å Fe is in a state close to the compensation point. (ii) Compared with the loops in fig. 9a, the loops in fig. 9b illustrate much better squareness because these samples were coated with a 500 Å SiO layer to protect from oxidation.

3.2.1.2. Temperature dependence of magnetic properties. Figure 11 is an example of the temperature dependence of the magnetic properties for Y Å Dy/6 Å Fe (Y=3, 5, 8, and 14). The discussion is simplified as follows. (i) The magnetization at 4.2 K is much larger than at 300 K since Dy is magnetically ordered at 4.2 K. (ii) At 4.2 K the samples usually possess a giant coercivity, e.g. $H_{c\perp} = 59$ kOe for 5 Å Dy/6 Å Fe and $H_{c\perp} = 37$ kOe for 14 Å Dy/6 Å Fe which is very weakly magnetically ordered at 300 K. The coercivity H_c of pure Dy film is about 10 kOe at 4.2 K. Therefore all the samples in fig. 10 have a coercivity larger than that of pure Dy films at 4.2 K. (iii) For all four samples, although $H_{c\perp} > H_{c\parallel}$ at 4.2 K, the anisotropy value is difficult to measure by torque magnetometry



Fig. 11. Hysteresis loops for Y Å Dy/6 Å Fe (Y = 3, 5, 8, and 14) at 300 K and 4.2 K (after Shan and Sellmyer 1990b).

because of the giant H_c value and by the hysteresis loops because of the impossibility to define an area between $\sigma_{\perp}(H)$ and $\sigma_{\parallel}(H)$ curves.

3.2.2. Dy/Co

3.2.2.1. Layer-thickness dependence of magnetic properties at room temperature. The hysteresis loops of 5 Å Dy/X Å Co and 3.5 Å Dy/X Å Co are shown in fig. 12 (Shan and Sellmyer 1990b). This figure shows that the magnetic anisotropy, magnetization, coercivity, and remanence change regularly as the Co and Dy layer thicknesses are changed, e.g. the coercivity H_c is relatively small for both small and large layer thicknesses, but it is large for intermediate values. Also the films possess perpendicular anisotropy for intermediate values.



Fig. 12. Co layer-thickness dependence of hysteresis loops for 5 Å Dy/X Å Co and 3.5 Å Dy/X Å Co at 300 K (after Shan and Sellmyer 1990b).

Figure 13 summarizes the layer-thickness dependence of the magnetization σ_{\perp} . Based on this systematic investigation, a three dimensional diagram is shown in fig. 14 which displays the main behavior of the magnetization. Several features should be pointed out. (i) The valley between the two peaks of magnetization, where $|\sigma_{\perp}|=0$, originates from the antiferromagnetic coupling of Co and Dy moments. Thus this valley traces the compensation points of the films of different compositions. The relationship between Dy and Co layer thicknesses for the compensation composition can be approximately expressed as $Y \simeq ({}^{13}\!/_{14})X$. (ii) The bigger peak of $|\sigma_{\perp}|$ on the right-hand side of the valley indicates a region where the Co magnetization dominates. The smaller hill of $|\sigma_{\perp}|$ on the left-hand side of the valley is the region where the Dy magnetization dominates. (iii) As the Co and Dy layers get very thin, the magnetization $|\sigma_{\perp}|$ approaches the behavior of homogeneous Dy–Co alloys because the "layers" are so thin that an almosthomogeneous amorphous alloy is formed.



Fig. 13. Layer-thickness dependence of magnetization for Y Å Dy/X Å Co at 8 kOe and 300 K. σ_{\perp} means the magnetization was measured with the applied field perpendicular to the film plane (after Shan and Sellmyer 1990b).

Fig. 14. Three-dimensional diagram of layer-thickness dependence of magnetization for Y Å Dy/X Å Co at 8 kOe and 300 K (after Shan and Sellmyer 1990b).

Figure 15 presents, in three-dimensional form, the layer-thickness dependence of the *intrinsic* anisotropy, $K_u = K'_u + 2\pi M_s^2$, where K'_u is the *measured* anisotropy (including the demagnetization every) and M_s is the saturation magnetization. There are several characteristics to be noticed: (i) The maximum value of K_u , where the sample exhibits the strongest perpendicular anisotropy, occurs at $X \sim 6$ Å, $Y \sim 6$ Å. (ii) As the Co layer gets thicker, K_u becomes negative (not shown in this figure for clarity); therefore the easy direction of magnetization becomes parallel to the film plane. (iii) The K_u peak becomes wider and lower as the Dy layer thickness increases, and K_u decreases rapidly



Fig. 15. Three-dimensional diagram of layer-thickness dependence of intrinsic anisotropy K_u for Y Å Dy/X Å Co at 300 K ($K_u = K' + 2\pi M_s^2$) (after Shan and Sellmyer 1990b).



Fig. 16. Hysteresis loops for 3.5 Å Dy/2.5 Å Co, 5.25 Å Dy/3.75 Å Co, 7 Å Dy/5 Å Co, 10.5 Å Dy/7.5 Å Co and 21 Å Dy/15 Å Co multilayers (after Shan et al. 1989).

and becomes negative (not shown in this figure for clarity) as the Dy layer gets very thin, since the amorphous Co-rich alloy has in-plane anisotropy.

A brief discussion, which may help to understand the magnetic structure of the Dy/Co, is given below. (i) Figures 12 and 15 show that the samples with intermediate layer thicknesses of X and Y exhibit strong perpendicular magnetic anisotropy. For example, (6 Å Dy)/(6 Å Co) has $(K_u)_{max}$ for layer thicknesses of Dy and Co of about 2 atomic layers, where the CMF has the maximum ratio of the "interface to volume". This means the "interfaces" of the CMF are responsible for the perpendicular magnetic anisotropy. The main feature of the interface is the anisotropic distribution of atoms there. In sect. 4.2 we will discuss the origin and calculation of the perpendicular magnetic anisotropy to put this argument on a more clear and solid foundation. (ii) A set of samples, (Y Å Dy)/(X Å Co) (Y/X = 3.5/2.5, 5.25/3.75, 7/5, and 21/15), was prepared. The shape of the hysteresis loops changed regularly as the nominal layer thicknesses of Dy and Co increased, as shown in fig. 16 (Shan et al. 1989). All five samples have the same chemical ratio of Dy and Co. This means that the behavior is clearly controlled by the layer thickness, consequently the distributions of Dy and Co atoms, rather than the chemical composition.

3.2.2.2. Temperature dependence of magnetic properties. Figure 17 shows the hysteresis loops for Y Å Dy/6 Å Co (Y = 3.5, 5, 8, 11, and 14) at 4.2 K and 300 K (Shan and Sellmyer 1990b). That the magnetic properties depend on temperature is clearly seen. (i) The magnetization of each sample at 4.2 K is larger than that at room temperature. Especially for 14 Å Dy/6 Å Co this feature is shown distinctly. (ii) The coercivity of each sample increases remarkably as the temperature decreases from 300 K to 4.2 K if we notice that the abscissa scale of fig. 17a is from -80 kOe to +80 kOe, which is ten times larger than that of fig. 17b. (iii) Both at 4.2 K and 300 K, sample 5 Å Dy/6 Å Co, whose layer thicknesses of Dy and Co are about 2-atomic diameter of each species, respectively, has the maximum values of anisotropy K_u . This also implies that the interface is the main source responsible for the anisotropy. (iv) At 4.2 K, the Dy moments are ordered and the coercivity $H_{c\parallel}$ (the coercivity for the applied field parallel to the film plane) increases as the Dy layer becomes thicker. This implies that the Dy atomic density has an important influence on the $H_{c\parallel}$.

Figure 18 summarizes the Dy layer-thickness dependence of magnetization and anisotropy at temperature T = 300 K and 4.2 K. The features (i) and (iii) mentioned above are found easily here and even more information can be obtained. (i) Antiferromagnetic coupling between Dy and Co magnetization is exhibited both at 300 K and 4.2 K, since the magnetizations change their sign as the Dy layer becomes thicker, and the compensation point moves from $Y \sim 6$ Å at 300 K to $Y \sim 4$ Å at 4.2 K. (ii) As the Dy layer thickness increases, the saturation magnetization $|\sigma_s|$ value gets larger at 4.2 K because the Dy moment becomes more dominant, but the $|\sigma_s|$ value decreases slightly at 300 K since the increase of Dy layer thickness will lead to magnetic disorder in the central part of the Dy region. (iii) The maximum value of K_u is about 1.4×10^7 erg/cm³ at 4.2 K and 2×10^6 erg/cm³ at 300 K, correspondingly. The K_u values at 4.2 K are much larger than those at 300 K. This feature suggests that the main origin of the anisotropy may be


Fig. 17. Hysteresis loops for Y Å Dy/6 Å Co at 4.2 K and 300 K (after Shan and Sellmyer 1990b).

related to a parameter which strongly depends on temperature, for example, the singleion anisotropy energy of Dy, which is proportional to the Dy subnetwork magnetization squared. A more detailed discussion of the origin of anisotropy will be given in sect. 4.2.

3.2.3. Tb/Fe

The magnetic properties of the Tb atom are similar to that of Dy: both have large atomic moments and single-ion anisotropy, etc. Thus many similarities between Dy/Fe and Tb/Fe CMF are expected. However, some differences also will be pointed out in the following discussion.



Fig. 18. Dy layer-thickness dependence of magnetization and anisotropy for Y Å Dy/6 Å Co at 300 K and 4.2 K (after Shan and Sellmyer 1990b).

3.2.3.1. Layer-thickness dependence of magnetic properties at room temperature. An example of the Fe layer-thickness dependence of hysteresis loops for (4.5 Å Tb)/(X Å Fe) with fixed Tb layer thickness of 4.5 Å is shown in fig. 19a and the corresponding Fe layer-thickness dependencies of magnetic parameters, such as magnetization and anisotropy, are given in fig. 20 (Shan and Sellmyer 1990b). The similarities between figs. 9a and 10 for (5 Å Dy)/(X Å Fe) and figs. 19a and 20 for (4.5 Å Tb)/(X Å Fe) are obvious. For example, sample (4.5 Å Tb)/(3.3 Å Fe) is close to the compensation point at room temperature, and there is a magnetization "kink" around X = 12 Å which is consistent qualitatively with the result reported by Honda et al. (1991b). Compared with Dy/Fe, Tb/Fe usually exhibits stronger perpendicular anisotropy and one example will be given in sect. 4.2.1.

Figure 19b (Shen 1994) shows the Dy layer-thickness dependence of hysteresis loops of Y Å Tb/5 Å Fe with fixed Fe layer thickness of 5 Å. We note the similarities between fig. 19b and 9b. Because the net magnetization increases with increasing Tb layer thickness, the Tb moments, which are induced by the Fe moments at room temperature, are dominant compared with the Fe moments.

3.2.3.2. Temperature dependence of magnetic properties. The magnetization, anisotropy and coercivity as functions of temperature for Y Å Tb/5 Å Fe (Y = 5, 5.5, 6, 6.5 and



Fig. 19. Fe layer-thickness dependence of hysteresis loops for (a) 4.5 Å Tb/X Å Fe (X = 2.5, 3.3, 3.75, 5, 6.25, 7.5, 8.75, 15, and 20) (after Shan and Selfmyer 1990b) and (b) Tb layer-thickness dependence of hysteresis loops for Y Å Tb/S Å Fe at 300 K (after Shen 1994).



Fig. 20. Fe layer-thickness dependence of magnetization and measured anisotropy for 4.5 Å Tb/X Å Fe at 300 K (after Shan and Sellmyer 1990b).

7 Å) samples are summarized in figs. 21, 22 and 23, respectively (Shen 1994). Since the individual layer thicknesses of both Tb and Fe layers are only about 2 atomic layers, it is reasonable to claim that the temperature dependent behavior exhibited in figs. 21–23 originates mainly from the strongly alloyed or interfacial regions: (i) We have pointed out before that Tb magnetization is dominant at room temperature for this



Fig. 21. Temperature dependence of magnetization for Y Å Tb/5 Å Fe (Y = 5, 5.5, 6, 6.5, and 7) (after Shen 1994).



Fig. 22. Temperature dependence of intrinsic anisotropy for Y Å Tb/5 Å Fe (Y = 5, 5.5, 6, 6.5, and 7) (after Shen 1994).

series of samples. As temperature decreases, the Tb magnetization increases because of the exchange interactions between Tb–Fe atoms and Tb–Tb atoms which implies that Tb atoms are getting further ordered magnetically with decreasing temperature. This



Fig. 23. Temperature dependence of coercivity for Y Å Tb/5 Å Fe (Y = 5, 5.5, 6, 6.5, and 7) (after Shen 1994).

behavior can be well interpreted with a mean-field model (Shan et al. 1990). (ii) The anisotropy K_u ($K_u = K'_u + 2\pi M_s^2$) increases with decreasing temperature and the sample with thinner Tb layer (Y = 5 Å) shows stronger temperature dependence. This behavior is also attributed to the enhancement of the Tb magnetization at lower temperature. (iii) As temperature decreases, the coercivity first increases slowly and then rapidly when the temperature is below ~100 K. It is found from the magnetization reversal study that the dominant mechanism of coercivity is domain wall pinning rather than nucleation; because the thermal activation energy decreases with decreasing temperature a larger applied field is required to cause magnetization reversal (Kirby et al. 1994). In sect. 5.1.3 this behavior will be discussed in more detail.

3.2.4. Interface anisotropy

In this subsection we discuss the experimental determination of interface anisotropy and show some typical results. For R/T multilayers, the R region is ordered magnetically at low temperature and from the energy viewpoint, the anisotropy energy per unit area can be written as

$$\lambda K'_{u} = 2K_{i}(T) + 2K_{i}(R) + [K_{v}(T) + K_{st}(T) + K_{de}(T)]X + [K_{v}(R) + K_{st}(R) + K_{de}(R)]Y,$$
(2)

where $\lambda = X + Y$ is the bilayer thickness, X and Y are the T and R layer thicknesses, respectively. K_i , K_v , K_{st} , K_{de} , represent the interface, volume, stress and demagnetization anisotropy for R and T, respectively. This is a rather complicated expression; however, at room temperature the R interior region is disordered magnetically which causes the fourth term in square brackets in eq. (2) to vanish, and then this equation is often simplified as

$$\lambda K'_{\rm u} = 2K_{\rm i} + [K_{\rm v} - 2\pi M_{\rm s}^2]X,\tag{3}$$

where $K_i = K_i(T) + K_i(R)$ is the sum of the T interface anisotropy and induced interface anisotropy of R layers; $K_v = K_v(T) + K_{st}(T)$ and $K_{de} = 2\pi M_s^2$. Figure 24 shows an example of $\lambda K'_u$ vs X for 8 Å Dy/8 Å Co at room temperature. This plot is helpful to discuss and understand the origin of PMA as follows: (i) It is often the case, for large X (X \ge 15 Å in this figure), that the $\lambda K'_u(X)$ data fall on a straight line with the slope and intercept equal to $[K_v - 2\pi M_s^2]$ and $2K_i$, respectively. (ii) The positive intercept implies that the interface anisotropy favors PMA which is the essential feature in multilayers, and the negative slope means that the demagnetization energy term dominates the K_v term, which may be positive at times. (iii) For small X (X \le 12 Å in this case), there is a general tendency for a maximum ($X \simeq 6$ Å in this case) to be seen in $\lambda K'_u$ and an approach to zero as $X \rightarrow 0$. This is understandable because this region corresponds to thicknesses less than a few monolayers, where it makes no sense to consider a well-defined volume and interface anisotropy. Moreover, the demagnetization energy will be ill defined. That $\lambda K'_u(X)$ goes to zero as $X \rightarrow 0$ is reasonable because the structure approaches that of a homogeneous, isotropic disordered alloy or glass. (iv) The reason that $\lambda K'_u$ maximum exists in the small X region $(X \simeq 6 \text{ Å}$ in this case) is that the microstructure of such CMF is similar to the interfaces in the CMF with large X, which shows positive interface anisotropy as pointed out in (iii).



Fig. 24. The measured anisotropy K' multiplied by the bilayer-thickness λ vs the Co layer-thickness for 8 Å Dy/X Å Co (after Shan and Sellmyer 1990b).

Figures 25 and 26 summarize the $\lambda K'_u(X)$ for Dy/Co and Nd/Fe CMFs. In both of these figures, the slopes of $\lambda K'_u(X)$ are negative and the intercepts are positive. Perera, O'Shea and Fert have prepared DyNi/Mo (Perera et al. 1991) and R/Mo (R = Dy, Er) (Perera and O'Shea 1991) multilayers and found similar $\lambda K'_u$ curves with negative slopes and positive intercepts as shown in fig. 27 for Er/Mo. This means that their PMA originates from the interface anisotropy. It is the single-ion anisotropy of R atoms and the anisotropic distribution of R and T atoms in the interface region which create the PMA.

Equation (3) can be rewritten as

$$K'_{\rm u} = \left[K_{\rm v} - 2\pi M_{\rm s}^2\right] \frac{X}{\lambda} + \frac{2K_{\rm i}}{\lambda}.$$
(4)

Ertl et al. (1992) employed this formula for Tb/Co multilayers with equal Tb and Co layer thickness (i.e. $2X = \lambda$) and eq. (4) becomes

$$K'_{\rm u} = \frac{K'_{\rm v}}{2} + \frac{K_{\rm i}}{X}, \qquad K'_{\rm v} = [K_{\rm v} - 2\pi M_{\rm s}^2].$$
 (5)

Therefore the curve of $K'_{u}(1/X)$ should be a straight line for small (1/X) (i.e. for large X) and bent for large (1/X) (i.e. small X). The result is shown in fig. 28. It is seen clearly



Fig. 25. Plot of $\lambda K'$ vs Co layerthickness for samples with Dy layerthickness Y=3.5, 5, 8, and 11 Å at 300 K (after Shan and Sellmyer 1990b).

Fig. 26. Plot of $\lambda K'$ vs Fe layerthickness for samples with Nd layerthickness Y = 7, 14 and 28 Å at 300 K (after Shan et al. 1988).



Fig. 27. Plot of $\lambda K'$ vs Er layer-thickness for X Å Er/10 Å Mo at 4.5 K. (Λ : bilayer thickness; t: Er layer thickness) (after Perera and O'Shea 1991).



Fig. 28. Plot of K' vs (1/X) for Tb/ Co CMF with equal Tb and Co layerthickness X at 300 K (d_L = Co or Tb layer-thickness) (after Ertl et al. 1992).

that K'_v is negative as determined from the intercept and K_i is positive determined from the slope. These results are consistent with what we have obtained from Dy/Fe, Dy/Co, Nd/Fe multilayers, as discussed above.

3.3. Mössbauer measurements

Mössbauer spectroscopy employing ⁵⁷Fe is a powerful tool to determine the magnetic structure for the Fe based alloys or multilayers. Following are some results of Mössbauer measurements for Tb/Fe, Dy/Fe and Nd/Fe multilayers.

3.3.1. *Tb/Fe*

3.3.1.1. Orientation of Fe moment. Determinations of the Fe moment orientation in Tb/Fe multilayers have been reported by Cherifi et al. (1991) and Scholz et al. (1991). Figures 29a,b show an example of Mössbauer spectra as a function of temperature



Fig. 29. (a) Mössbauer spectra collected at different temperatures T: (1) T = 4.2 K, (2) T = 90 K, (3) T = 200 K, (4) T = 300 K from a sample 17 Å Tb/33 Å Fe fabricated at substrate temperature $T_s = 90$ K. (b) Mössbauer spectra collected at: (1) T = 4.2 K, (2) T = 90 K, (3) T = 300 K, (4) T = 420 K from a sample 39 Å Tb/40 Å Fe fabricated at $T_s = 420$ K (after Cherifi et al. 1991).

for 17 Å Tb/33 Å Fe and 39 Å Tb/40 Å Fe which are fabricated at substrate temperature $T_s = 90$ K and 420 K, respectively. As is well known, the orientation of Fe moment can be determined from the intensities of peaks 2 and 5 of the Fe component in the 3:X:1:1:X:3 ratio with $X = 4 \sin^2 \Theta/(1 + \cos^2 \Theta)$ where Θ is the angle between the γ -ray direction, which is perpendicular to the film plane, and direction of the Fe magnetic moments. Therefore X = 4 ($\Theta = \pi/2$), 0 ($\Theta = 0$) and 2 ($\Theta = 54.73^{\circ}$) correspond to the cases where the Fe moments are in the plane, perpendicular to the plane and in a random orientation, respectively. The temperature dependence of Fe moment orientations is shown in fig. 30. It shows that as the temperature varies from 4.2 K



Fig. 30. Thermal evolution of the angle between the average direction of magnetic moments and the film normal: (a) 17 Å Tb/33 Å Fe at $T_s = 90 \text{ K}$ (solid circle); (b) 39 Å Tb/40 Å Fe at $T_s = 420 \text{ K}$ (solid diamond). The random orientation corresponds to $\Theta = 54.73$ (after Cherifi et al. 1991).

to 300 K, the angle Θ between the Fe moments and the film normal increases from 30° to 80° for 17 Å Tb/33 Å Fe and is nearly independent of temperature below 300 K for 39 Å Tb/40 Å Fe. If the temperature increases further to 420 K, Θ approaches 90° for 39 Å Tb/40 Å Fe as well.

3.3.1.2. Interfacial magnetism. Cherifi et al. (1991) concluded that the effect of alloyed interfaces resulting from heated substrates enhances the perpendicular magnetic anisotropy (PMA). This seems in conflict with the conventional concept that the film fabricated at lower substrate temperatures possesses sharper interface boundaries and consequently will show larger PMA. Our understanding is that the sharper boundaries alone are not sufficient to generate larger PMA; both structural anisotropy (i.e., sharper boundaries) and appropriate interactions are required to produce PMA. In this example the enhancement of PMA from the increasing interaction due to the alloy effect overcomes the reduction of PMA resulting from the more diffused boundaries. This feature will be discussed in more detail in sect. 4.2.2.

Cherifi et al. (1991) pointed out that the Mössbauer spectra in fig. 29a cannot be fitted by a unique sextuplet of bcc Fe absorption peaks, and a residual component representing 40% of the area, which means 6 Å of Fe at each interface, can be isolated by subtracting the bcc peaks as shown in fig. 31a, b. We notice: (i) the hyperfine field distribution in fig. 31b is very asymmetrical with a tail on the low field side. (ii) The residual spectra exhibit a similar temperature evolution as in fig. 29a. (iii) The residual spectra do not show PMA at T = 200 K and 300 K as one might have expected. Our understanding is that the interior layer of Fe, which possesses much larger Fe moments compared to the Fe moments in the interface region and exhibits in-plane anisotropy, forces the Fe moments in the interface to lie in the film plane because of the exchange interaction.

Badía et al. (1991) have reported Mössbauer studies on Tb/Fe. These authors found: (i) the thickness of interface deduced from the distribution of hyperfine fields is about 2 monolayers of Fe (i.e., ~ 5 Å) and this would mean that for sample 26 Å Tb/10 Å Fe

NANOSCALE R/T MULTILAYERS



Fig. 31. (a) Residual contributions to spectra of fig. 29a attributed to the interfaces, obtained after subtracting the pure Fe components; (b) corresponding hyperfine field distribution (after Cherifi et al. 1991).

almost all of the Fe layers are alloyed with Tb. (ii) Three samples of 26 Å Tb/X Å Fe (X = 10, 20, 30), show PMA at 4.2 K, but only 26 Å Tb/10 Å Fe samples show PMA at 300 K. This may be regarded as evidence that interfacial magnetism favors PMA. (iii) Sample 7 Å Tb/40 Å Fe shows PMA, but 26 Å Tb/30 Å Fe does not. The most important difference between them is that the former does not have single Tb layers and thus the authors conclude that the single Tb layer is not the origin of the perpendicular anisotropy but the presence of the alloying at the interfaces.

The antiferrimagnetic coupling between Tb and Fe moments has been studied by Mössbauer spectra measured in an external field (Scholz et al. 1991). As can be seen from fig. 32, we obtain an *increase* of the effective hyperfine field with external field independent of its orientation $(B_p(4.2 \text{ K}, 5 \text{ T})=3.27 \text{ T})$, where B_p is the peak value of the hyperfine field); this means that Tb aligns preferentially along the external field direction, and that Fe and Tb moments are on the average antiparallel, similar to Fe–Tb alloys.



Fig. 32. Comparison of Mössbauer spectra and hyperfine field B_{hf} distributions at 4.2 K obtained in (a) $B_{ext} = 0$ T, (b) $B_{ext} = 5.0$ T perpendicular to the film plane (after Scholz et al. 1991).



Fig. 33. (a) Temperature dependence of Mössbauer spectra for 6 Å Dy/33 Å Fe; (b) temperature dependence of the average angle Θ between the film plane and the spin direction of Fe estimated from the Mössbauer spectra of (a) (after Yoden et al. 1988).



Fig. 34. Mössbauer spectra at 300 K (A) and 4.2 K (B) for samples with fixed Fe layer thickness of 39 Å: (a) 46 Å Nd/39 Å Fe, (b) 28 Å Nd/39 Å Fe, (c) 10 Å Nd/39 Å Fe, and (d) 7 Å Nd/39 Å Fe (after Mibu et al. 1989).

3.3.2. Dy/Fe and Nd/Fe

Mössbauer measurements for Dy/Fe and Nd/Fe have been performed by several authors. Figure 33a shows an example of the temperature dependence of Mössbauer spectra for 6 Å Dy/33 Å Fe, and its Θ angle as a function of temperature is given in fig. 33b (Yoden et al. 1988). It is seen that the Fe moment direction changes from more perpendicular at 4.2 K to more in plane at 300 K. Figure 34 (Mibu et al. 1989) shows examples of Mössbauer measurements for Y Å Nd/39 Å Fe (Y = 46, 28, 10, 7) at 300 K and 4.2 K. It is seen that at 4.2 K all samples show PMA, but at 300 K only two samples of 10 Å Nd/39 Å Fe and 7 Å Nd/39 Å Fe have PMA, and the temperature dependences of X (here X is the relative intensity of the 2nd and 5th peaks) and Θ are given in fig. 35 for sample 28 Å Nd/39 Å Fe. A further discussion of these results is given in the references cited above.

3.4. Magnetic circular X-ray dichroism measurements

Magnetic circular X-ray dichroism (MCXD) allows one to deduce direct information of local magnetic moments, anisotropy behavior, and characteristics of interface magnetism.



Fig. 35. Temperature dependence of relative intensity X of the 2nd and 5th Mössbauer absorption lines for 28 Å Nd/39 Å Fe. The corresponding angle Θ between the direction of Fe moments and the film normal is also indicated on the right side of the ordinate (after Mibu et al. 1989).

MCXD, unlike Mössbauer measurements which show only the Fe magnetic structure directly (if the ⁵⁷Fe source is used), can be used to investigate the magnetic structure of almost all the elements. This is an important advantage.

MCXD studies on Tb/Fe and Nd/Fe multilayers have been reported. However, only the results for the Tb/Fe multilayer (Attenkofer et al. 1993) are presented here because of space limitations. The reader can find information for Nd/Fe in the article by Baudelet et al. (1991).

The samples used for MCXD are 26 Å Tb/X Å Fe (X = 10, 20, 30 and 35) and examples of magnetic (μ_c/μ_0) spectra for Tb and Fe are shown in figs. 36 and 37; here $\mu_c = \mu^+ - \mu^-, \mu_0 = \mu^+ + \mu^-$ and $\mu^+(\mu^-)$ is the absorption coefficient for an antiparallel (parallel) orientation of photospin relative to the magnetization direction of the sample. The following results were obtained from the MCXD spectra.

(A) The magnetic moment of Tb and the anisotropy behavior for the different samples are shown in table 2 where Θ is the angle between film normal and the photon beam direction. The sign (i.e., + or –) of μ_{Θ} reflects directly the orientation of the Tb moment relative to the applied magnetic field. For an Fe layer thickness of 10 Å the orientation is parallel (+ sign) and changes sign for the multilayer with an Fe layer thickness of 35 Å, indicating that a compensation thickness is reached at ~25 Å Fe.

(B) Compared with the magnetic (μ_c/μ_0) spectra of Tb L₃, the corresponding magnetic (μ_c/μ_0) spectra of the Fe K-edge shows an opposite behavior, reflecting directly the antiparallel coupling of the Fe and Tb layer as expected.



Fig. 36. Magnetic μ_c/μ_0 spectra at the Tb L₃ (upper panel) and L₂ (lower panel) of TbFe₂, 26 Å Tb/35 Å Fe and 26 Å Tb/10 Å Fe multilayered structures, and Tb-metal (after Attenkofer et al. 1993).



Fig. 37. Magnetic μ_c/μ_0 spectra at the Fe K of TbFe₂, 26Å Tb/35Å Fe and 26Å Tb/10Å Fe multilayered structures, and Fe-metal (after Attenkofer et al. 1993).

Table 2 Magnetic moment of Tb for the different multilayer (ML) samples (for the definition of Θ see text)

ML sample	$\mu_{\Theta} = 0^{\circ} (\text{Tb}) (\mu_{B})$	$\mu_{\Theta} = 30^{\circ} (\text{Tb}) (\mu_{B})$	$\mu_{30^{\circ}}/\mu_{0^{\circ}}$ (Tb)
26Å Tb/10Å Fe	+1.4(0.1)	+0.8(0.3)	+0.57(0.22)
26Å Tb/20Å Fe	+0.7(0.2)	+0.6(0.2)	+0.86(0.38)
26Å Tb/30Å Fe	-1.3(0.8)	-1.4(0.2)	1.08(0.68)
26Å Tb/35Å Fe	-2.1(0.6)	-2.6(0.5)	1.24(0.43)

(C) From the ratio of $(\mu_{30^{\circ}}/\mu_{0^{\circ}})$ we find that the anisotropy changes from PMA for samples with thinner Fe layers to in-plane anisotropy for samples with thicker Fe layers.

(D) Since the magnetic (μ_c/μ_0) spectra at the Tb L₂-edge and the Fe K-edge are sensitive to the local chemical environment, one may use this feature to obtain information on the magnetic structure of the interface region where the local chemical environment of Tb (or Fe) atoms is significantly different from that of pure Tb (or Fe) metals. The magnetic (μ_c/μ_0) spectra at the Tb L₂-edge are shown in the lower part of fig. 36. Comparing the 26 Å Tb/35 Å Fe, 26 Å Tb/10 Å Fe with the intermetallic compound TbFe₂ and the pure Tb-metal, changes in the spectra can be observed. Comparing the labeled features B, C, D (in fig. 36), in TbFe₂, the multilayer, and the Tb-metal spectra, a linear variation of the amplitudes, as indicated by the dotted lines, can be obtained. A similar behavior is found for the maximum A in the Tb L₃ spectra. These changes of the MXCD spectra indicate that significant contributions to the magnetism come from the interface region whose chemical structure resembles that of the intermetallic compound TbFe₂.

4. Theoretical model for magnetization and anisotropy

4.1. Magnetization distribution

The existence of the compositional modulation of R and T constituent atoms offers an extra degree of freedom to control the local atomic environments which permits the tailoring of magnetic properties, such as PMA, in artificially structured CMF. However, this also introduces a new problem in determining the magnetization distribution which originates from the compositional modulation along the film-normal direction. The magnetization distribution in CMF was determined in the following way.

The compositional dependence of magnetizations (the R-, T-subnetwork magnetization and total magnetization) for homogeneous R-T alloys can be performed by using the mean-field model (Hasegawa 1975, Shan and Sellmyer 1990b). Figure 38 shows an example for $Dy_{1-x}Co_x$ alloys. In addition to the total magnetization σ , the Co- and Dysubnetwork magnetizations σ_{Co} and σ_{Dy} , are presented.

The method of determining the magnetization distribution in R/T CMF was discussed by Shan et al. (1990). The R/T film is divided into thin slices, each of which can be regarded as a two-dimensional amorphous film. A distribution of T (or R) concentration, e.g. a sinusoidal function

$$\eta_j(z) = A_{j0} \pm A_j \sin\left(\frac{2\pi Z}{\lambda}\right) \tag{6}$$

is assumed for the thin layer-thickness CMF (for the purpose of this derivation we assumed R and T have equal thickness for simplicity). Here j=1 and the + refer to T, j=2 and the - refer to R and the Z axis is along the film normal. A_{j0} is a constant and A_j



Fig. 38. Co concentration dependence of spontaneous magnetization for Dy–Co alloys: the total magnetization σ_s , Dy-subnetwork magnetization σ_{Dy} , and Co-subnetwork magnetization σ_{Co} (after Shan et al. 1990).

the modulation amplitude of the *j*th constituent concentration. As we have pointed out in sect. 3.1, the small angle X-ray diffraction for the multilayers with thin layers ($\lambda < 15$ Å) shows only the first-order peaks; therefore it is reasonable to assume the sinusoidal function of eq. (6) for the compositional modulation.

The T concentration of the *i*th slice with coordinates Z_i is $\eta_1(Z_i)$ determined from eq. (6) and consequently its magnetization σ_i , σ_{1i} , σ_{2i} can be obtained from fig. 38 if we assume R=Dy and T=Co. Thus, the average magnetization σ of the CMF is equal to

$$\sigma = \frac{1}{\lambda} \sum_{i} \sigma_i \Delta Z_i = \frac{1}{\lambda} \sum_{i} (\sigma_{1i} - \sigma_{2i}) \Delta Z_i.$$
⁽⁷⁾

The parameters of the distribution function, i.e. A_{jo} and A_j , were adjusted until the σ value calculated from eq. (7) fitted the experimental data within a certain error. We point out that the constraints corresponding to the conservation of total number of R or T atoms must be satisfied while adjusting the parameters A_{jo} and A_j .

Figures 39a,b show an example of the distributions of (a) Co concentration and (b) magnetization for 6 Å Dy/6 Å Co. It is seen that σ_{Dy} dominates in the Dy region and σ_{Co} dominates in the Co region, as is reasonable.

Figure 40 shows the Co layer-thickness dependence of the average values of the total magnetization σ , Co- and Dy-subnetwork magnetization σ_{Co} and σ_{Dy} (fig. 40a) and the Co-atomic fraction modulation "A", i.e. A_1 in eq. (6) (fig. 40b). It is seen that the calculated σ value agrees with the experimental data quite well; the A value is only about 0.1 for the thinnest Co layer thickness of 3.5 Å and its value increases as Co layer becomes thicker. The data shown in fig. 40 will be used to illustrate the calculation of the magnetic anisotropy.



Fig. 39. Co concentration distribution (a) and magnetization distribution (b) along the film normal for 6\AA Dy/ 6\AA Co (after Shan et al. 1990).

Fig. 40. Comparison of the calculated magnetization with the experimental data for (a) 6 Å Dy/X Å Co (X = 3.5, 5, 6, 8, 10, and 11), and (b) the Co layer-thickness dependence of the Co atomic fraction modulation (after Shan et al. 1990).

4.2. Perpendicular magnetic anisotropy (PMA)

4.2.1. The origin of PMA in R/T

Many efforts have been made to investigate the magnetic anisotropy and its origin in thin films. Hellman and others have listed various sources of PMA (Hellman et al. 1989, Hellman and Gyorgy 1992) including pair ordering, local clusters, bond-orientationalanisotropy (BOA) (Yan et al. 1991), stress anisotropy, anisotropy due to columnar microstructure, surface anisotropy due to magnetic dipolar origin and the growth-induced anisotropy, etc. Suzuki et al. (1987) and Baczewski et al. (1989) suggested that the singleion anisotropy of the R atom contributes to PMA. After analyzing the function of various sources carefully, it is necessary to specify both the details of the *structural anisotropy* and the nature of the *magnetic interactions*.

(A) Structural anisotropy, i.e. the anisotropic distribution of the constituent atoms, is generated by (i) the artificial multilayered structure which follows from the fabrication procedure, (ii) the crystal structure for the crystalline R (or T) layers, or (iii) any other sources of anisotropic pair correlations such as those listed in the previous paragraph.

Harris and coworkers (1992, 1993) have performed an important study on the structural origin of PMA in sputtered amorphous Tb-Fe films. These authors performed extended X-ray absorption fine structure (EXAFS) measurements to study the anisotropic shortrange structure. X-ray absorption spectra for both Fe K and Tb L₃ absorption edges were obtained with synchrotron radiation and fig. 41 (Harris et al. 1993) shows the Fourier transformed EXAFS data for Fe and Tb. These data show a distinct difference in the amplitudes for electric fields parallel and perpendicular to the film. The data show that the coordination numbers are different for the two different orientations and in fact show that there is an excess number of Fe-Fe and Tb-Tb pairs in the plane of the film and an excess of Tb-Fe pairs perpendicular to the plane of the film. This is shown qualitatively in typical atomic arrangements in fig. 41. Moreover, Harris et al. heat treated one of their samples, Tb_{0.26}Fe_{0.74}, at 300°C for one hour and the resulting Fourier-transformed EXAFS amplitude shows that the structural anisotropy seen in fig. 41 has been reduced by the annealing. The authors thus suggest that the high temperature annealing has removed most of the anisotropic pair correlations and the remaining anisotropy which is perhaps 20% of the original is likely to be due to magneto-elastic interactions between the film and the substrate. The work of Harris et al. can be regarded as direct evidence that the structural anisotropy is one of the necessary conditions to create PMA. This work thus confirmed that the structural anisotropy in the interface region of multilayers is an excellent method for producing PMA.

(B) Magnetic interactions leading to anisotropy include mainly the following two: (i) magnetic dipolar interactions and (ii) spin-orbit interactions which lead to singleion anisotropy associated with lanthanide atoms. Single-ion anisotropy arises from the interaction between the 4f electrons of the R atoms and the local electric field created by the neighboring ions. If the charge distribution of the 4f electrons is nonspherical, i.e. $L \neq 0$, the electric field forces the 4f electrons, the orbital momentum of the 4f electrons and consequently the magnetic moment into a preferred orientation, i.e.



Fig. 41. (a) Fourier transformed Fe EXAFS data, (b) Tb EXAFS data collected using normal incident photons (solid lines) and glancing incident photons (dashed lines). Plot insets illustrate the schematic diagrams of typical atomic arrangements in R-T amorphous alloys where anisotropic pair correlations are shown (after Harris et al. 1993).

the easy magnetizing direction, through the strong spin-orbit coupling. Therefore both a structural anisotropy as discussed above and the interaction between the 4f electrons of R atoms and the local crystal field are the major origins of magnetic anisotropy in R/T multilayers for those R atoms with orbital angular momentum.

For Gd–Co homogeneous films, Mizoguchi and Cargill (1979) have calculated the magnetic anisotropy in terms of the dipolar interaction for the samples with a short-range anisotropic microstructure. Fu et al. (1991) have shown that the magnetic dipolar interaction in the surface layers contributes to the intrinsic PMA. The calculated PMA based on dipolar interactions is of the order 10^3-10^4 erg/cm³ for amorphous Gd–Co films which is much smaller than that of PMA in R/T (R=Tb, Dy; T=Fe, Co). However, Hellman and Gyorgy (1992) argued reasonably that the surface dipolar interactions considered by Fu et al. are not an important source of anisotropy in R–T films containing heavy lanthanides with orbital angular momentum. Theoretical calculations of Jaswal (1992) also came to the same conclusion.

Figure 42 illustrates our experimental results for the K_u behavior of R/T (R=Tb, Dy, Gd and T=Fe, Co). This figure demonstrates that the anisotropy K_u for Dy/Fe, Dy/Co,



Fig. 42. Anisotropy for 4.5 Å Tb/X Å Fe, 5 Å Dy/X Å Fe, 6 Å Dy/X Å Co, and Gd/Fe CMFs. The anisotropy data of 2.3 Å Gd/3 Å Fe, 3 Å Gd/3 Å Fe, 3 Å Gd/5 Å Gd, etc., are in the shaded area (after Shan et al. 1990).

and Tb/Fe is roughly an order of magnitude larger than that of Gd/Fe. Since, to first order, the Gd atoms have no single-ion anisotropy, it is reasonable to attribute the main origin of the PMA of the Dy and Tb CMF to single-ion anisotropy of Dy and Tb atoms which are located in the interface regions.

Mibu et al. (1993) prepared 30 Å R/40 Å Fe multilayers (R=Pr, Nd, Tb, Dy, etc.) for Mössbauer studies. The Mössbauer spectra indicate that the Fe moments lie in the film plane at 300 K but turn to the perpendicular direction at lower temperatures. Since all these R atoms have similar 4f electron distribution, the authors concluded that the 4f electron of R atoms should be responsible for the PMA at lower temperatures.

As outlined above it is clear that for the R/T where R atoms have orbital angular momentum, the PMA results from the single-ion anisotropy of R atoms and structural anisotropy in the interface region. In the next subsection, a theoretical expression for PMA is derived based on this concept. It is also essential to point out that the stress anisotropy and BOA have been involved in the PMA induced by the distortion of the structure from the strains in the films. Once the distorted structure is determined, this will then affect the magnitude of both the structure anisotropy and the interactions among all R and T atoms and consequently the PMA behavior.

4.2.2. PMA model for R/T

Shan et al. (1990) have developed a theoretical model of PMA in R/T. Figure 43 shows the local environment of an R atom (Dy in this case) atom in the vicinity of an "interface" of the CMF. For the *i*th slice of the CMF, the local single-ion anisotropy is given by

$$K(i) \propto \alpha_{\rm J} \left\langle r^2 \right\rangle O_2^0 A_2^0, \tag{8}$$



Fig. 43. (a) Crystal field created by the neighbor ions, (b) local anisotropy K(i) at Z_i . The resultant anisotropy K_u is the average of K(i) over the whole volume of CMF. (c) Concentration distribution C_j (j = 1 refers to Co, j = 2 refers to Dy) along the film normal (after Shan et al. 1990).

where α_J is Stevens' factor; $\langle r^2 \rangle$ is the average radius squared of the 4f orbit, O_2^0 is Stevens' operator O_n^m with n=2 and m=0. O_2^0 is a factor proportional to J_z^2 if Z is the easy-axis direction. A_2^0 is a crystal-field term given by

$$A_2^0 \propto \sum_j \frac{q_j(3\cos^2\Theta_j-1)}{r_j^3}.$$

Upon substitution eq. (8) then becomes

$$K(i) \propto \alpha_J \left\langle \sigma_z^2 \right\rangle_i \sum_j \frac{q_j (3\cos^2 \Theta_j - 1)}{r_j^3},\tag{9}$$

where j is the index of the jth ion in the neighborhood of the R ion at the ith slice. The summation is over the neighboring ions with charge q_j and distance r_j from the R ion and Θ_j is the angle with respect to the moment direction (see fig. 43). The average notation $\langle \rangle_i$ means the statistical average of the R ion over the *i*th slice. In the above derivation, the relation, $\sigma_Z \propto J_Z$, has been used, where σ_Z and J_Z are the Z component of R subnetwork magnetization and angular momentum, respectively.

For the amorphous CMF structure the sum over j in eq. (9) must be replaced by an integral weighted with an anisotropic probability function. This function for a CMF structure may be expressed as

$$P_{ij}(r) = \eta_j R_j(r) \left[1 + \beta_j(r) \cos \alpha_j + \cdots \right], \qquad (10)$$

where η_j is the atomic fraction of the *j*th surrounding ion consisting of R and T ions which have the sinusoidal form as shown in eq. (6). $R_j(r)$ gives the isotropic part of the distribution, while $\beta_j(r)$ is the lowest-order anisotropic contribution. The parameter β_j , the anisotropy in the pair distribution function, is determined by the inherent structure built into the multilayer, and also structural inhomogeneities produced by chemical shortrange order or stress at the interfaces. α_j is the angle between r_j and the film normal Z as shown in fig. 43b.

In the CMF structure η_i varies along the film normal so that

$$P_{ij}(r) \simeq \left[\eta_j(Z_i) + \eta'_j(Z_i)r\cos\alpha_j\right] R_j(r) \left[1 + \beta_j(r)\cos\alpha_j\right],\tag{11}$$

where the relation $\Delta Z_i = r \cos \alpha_j$ is adopted, i.e. the R ion at the *i*th slice is assumed to be the origin of the spherical coordinate and the polar axis is along the Z direction, i.e. the film normal direction. η'_i is the first derivative of η_j .

Then the local anisotropy K(i) of a R ion at the *i*th slice is

$$K(i) \propto \alpha_J \langle r^2 \rangle \langle \sigma_z^2 \rangle_i \int \frac{(3\cos^2 \Theta_j - 1)\rho_j}{r_j^3} P_{ij}(r) \,\mathrm{d}\Omega_j$$

$$\propto K_0 \langle \sigma_z^2 \rangle_i \left[\frac{A_j}{\lambda}\right] \cos\left[\frac{2\pi Z_i}{\lambda}\right], \qquad (12)$$

where

$$K_{0} = \alpha_{J} \left\langle r^{2} \right\rangle \left[\frac{\rho_{1} R(r_{1}) \beta_{1}}{r_{1}^{2}} - \frac{\rho_{2} R(r^{2}) \beta_{2}}{r_{2}^{2}} \right].$$
(13)

In the above derivation, the integral is calculated over the neighboring atoms with charge density ρ_j and distance r_j from R ion, usually nearest-neighbor atoms only, and ρ_j , $R(r_j)$, and β_j are assumed to be different, but constant for the T(j=1) and R(j=2) ions.

The anisotropy K_u of the R/T CMF can be obtained as the average of K(i) over all the slices as shown in fig. 43b. If the magnetization σ_z changes smoothly along the film normal, which is true for the sample with thin layer thickness, K_u can be written as

$$K_{\rm u} = \xi \left\langle \sigma_z^2 \right\rangle \left[\frac{A}{\lambda} \right]. \tag{14}$$

Equation (12) shows that the local anisotropy K(i) is proportional to $\cos(2\pi Z_i/\lambda)$: since the cosine function has its peak value at $Z_i = 0$, i.e. the nominal boundary position, the

interface region will give the main contribution to the anisotropy. Equation (14) shows that the larger value of A/λ , which can be understood as the average of the compositional modulation, favors a larger perpendicular magnetic anisotropy. Equation (14) also shows that a larger average of R subnetwork magnetization squared, $\langle \sigma_z^2 \rangle$, favors a larger PMA. Since pure R (Dy, Tb, Nd, etc.) is magnetically disordered at room temperature, it is the exchange interaction between T and R in the interface region that makes R magnetically ordered. Therefore the interface mixing, which may increase the nearest T neighbors for the R atom and thus increases R subnetwork magnetization, will enhance the PMA value. This feature has been observed in sect. 3.3.2 for Tb/Fe Mössbauer spectra. Equation (13) shows that K_0 is associated with $\beta_j(j=1 \text{ or } 2)$ which is related to the short-range anisotropic distribution of R and T ions. Therefore the K_u will depend on the preparation conditions which give the effects on the short-range anisotropic distributions.

4.2.3. Analysis for Dy/Co and Tb/Fe

The intrinsic anisotropy K_u , which is expressed with eq. (14), is fitted to the K_u data for (6 Å Dy)/(X Å Co) with ξ as an adjustable parameter and the results are shown in fig. 44a. The agreement between the experimental data and calculated results is remarkable. The fitted value of $\xi = 5.26 \times 10^{-6}$ cm leads to an average value of the single-ion anisotropy parameter $D = 2 \times 10^{-17}$ erg, which is reasonable in terms of the typical value of the single-ion random-anisotropy parameter in amorphous alloys. The good agreement between the calculated and experimental data further confirms the suggestion that the Dy ion anisotropy plus the structural anisotropy in the interface region is the major source of perpendicular anisotropy is reasonable. This also can be found intuitively from the fact that the $\langle \sigma_{Dy} \rangle$ curve in fig. 40a is similar to the K_u curve in fig. 44a and the $\langle \sigma_{Co} \rangle$ curve in fig. 40a has a totally different shape which hints the Co subnetwork magnetization cannot be the origin of PMA.

Figure 44b shows the Fe layer-thickness dependence of intrinsic anisotropy for Tb/Fe. The calculated data agree with the experiment fairly well. This result also implies that the model developed in this section is reasonable.



Fig. 44. Comparison between the calculated and experimental anisotropy for (a) 6 Å Dy/X Å Co (X = 3.5, 6, 8, 10, and 11) and (b) 4.5 Å Tb/X Å Fe (X = 2.5, 3.3, 3.75, 5, 6.25, 7.5, and 8.75) (after Shan et al. 1990).

4.2.4. *PMA* for Gd/T (T = Co, Fe)

The fact that Gd–T alloys or Gd/T multilayers show PMA is well known. Since, to first order, the Gd ion in its ground state has no orbital angular momentum (i.e. $L \approx 0$), it has been considered that single-ion anisotropy is not the major source of PMA for Gd/T. This would imply that dipolar interactions plus atomic short-range structural anisotropy for Gd–T alloys or structural anisotropy in the interface region for Gd/T are the main origins of PMA (Mizoguchi and Cargill 1979). However, the PMA in Gd/T is about 10^{4} – 10^{5} erg/cm³ which is about 10–100 times smaller than that of R/T (R=Tb, Dy, Nd). In this case the structural anisotropy plus the single-ion anisotropy from the unquenched Coorbital momentum (Y. Wu et al. 1992, Y.J. Wang and W. Kleemann 1992) or from the mixing effect of Gd states with orbital angular momentum (O'Shea et al. 1983, Wybourne 1966) also may give an appreciable or even dominant contribution. This is a remaining problem for further study.

4.2.5. Magnetic anisotropy for Dy/M (M = Ta, Cu and Y)

Dy/M CMF where M is the nonmagnetic metals (M=Ta, Cu, Y), have been investigated, and none of them show PMA at 5 K (Shan et al. 1991). Such behavior may be interpreted in terms of eq. (14). Since Ta, Cu and Y are nonmagnetic metals, the magnetization comes wholly from the Dy subnetwork and their Dy-subnetwork magnetization σ_{Dy} is smaller than in the R/T case. In the case of Dy/Ta, even though A/λ is larger than that of Dy/T (T=Co, Fe), σ_{Dy} for Dy/Ta is much smaller compared to that of Dy/T. In the case of Dy/Cu and Dy/Y, both σ_{Dy} and A/λ are smaller compared with Dy/T. In consequence, the Dy/M CMFs discussed here never show PMA.

In summary, a detailed model has been developed to understand the occurrence and control of PMA in R/T CMF. The single-ion anisotropy of the R ion, which has orbital angular momentum, in the interface region gives the major contribution to PMA because the structural anisotropy of interfaces offers a crystal field to force the R magnetic moment preferably into the film normal direction through the spin–orbital coupling. The total and constituent magnetizations are determined in this model as well. The experimental data only show the magnetic properties resulting from a statistical average over the whole sample; however, the modeling analysis permits the determination of more information on the concentration and magnetization distributions.

5. Magnetization reversal and microscopic effects

5.1. Magnetization reversal

The most common experimental approach to study the magnetization reversal is to measure the time dependence of the magnetization (or Kerr rotation angle) near the coercivity field. We summarize here the results of such measurements for Tb/Fe and Dy/Fe and discuss a newly developed model proposed by Kirby et al. (1994).



Fig. 45. Time dependence data for 14.3 Å Tb/8.5 Å Fe of 32 bilayers at various applied fields (after O'Grady et al. 1994).

5.1.1. Tb/Fe

A model first presented by Street and Woolley (1949) has been widely used to interpret measurements of the time decay of magnetization. This model presumes that reversal occurs by thermal activation over an energy barrier which has a broad distribution of barrier heights. Street and Woolley showed that this assumption leads to a time dependence of magnetization M(t) given by

$$M(t) = M(0) + S(H)\ln(t) \qquad \text{for intermediate } t, \tag{15}$$

where S(H) is the magnetic viscosity and H is the applied field. Equation (15) is only valid for a broad and uniform distribution of barrier heights. Other non-uniform distributions lead to deviations from ln(t) behavior.



Fig. 46. Activation volumes for $(14.3 \text{ Å Tb}/8.5 \text{ Å Fe}) \times n$, where *n* is the number of bilayers (after O'Grady et al. 1994).

The magnetic viscosity is related to the irreversible susceptibility $\chi_{irr}(H)$ by O'Grady et al. (1993, 1994).

$$H_{\rm f} = \frac{k_{\rm B}T}{\upsilon M_{\rm s}} = \frac{S(H)}{\chi_{\rm irr}(H)},\tag{16}$$

where $H_{\rm f}$ is the fluctuation field, v is the activation volume for reversal and $M_{\rm s}$ is the saturation magnetization.

The magnetic viscosity S(H) can be determined from the slope of the M(t)-ln(t) curve and is found to vary with the field, generally going through a maximum in the vicinity of the coercivity. The activation volume v is also determined experimentally because both S(H) and $\chi_{irr}(H)$ can be obtained from the time decay curves and remanence curves, respectively. O'Grady et al. (1994) used the above analysis to study the magnetization reversal in (14.3 Å Tb/85 Å Fe) as a function of the number of bilayers. The time decay curves for a sample with 32 bilayers is shown in fig. 45 and the activation volumes as a function of bilayer number in fig. 46.

O'Grady et al. (1994) interpreted their results in terms of a two-coercivity model. The main idea in this approach is that there are two fields H_N and H_{DW} , representing the nucleation and domain wall critical fields, respectively. For a film in which $H_N > H_{DW}$, the hysteresis loop will be square since a reversed domain will expand immediately after the nucleation. If, however, $H_{DW} > H_N$, reversed domains will be formed and be subject to wall pinning. This will lead to a rounded loop. O'Grady et al. (1994) also pointed out that (i) the isothermal remanence magnetization (IRM) curve determines the distribution of H_{DW} since it begins from a state in which domains are present in both directions and (ii) the DC demagnetizing remanence magnetization (DCD) curve



Fig. 47. (a) IRM and DCD differentials for 14 bilayer sample and (b) for 28 bilayer sample (after O'Grady et al. 1994).

determines the distribution of H_N since it begins from a state previously saturated. The differential of the IRM curve, $\chi_{irr}^i(H)$, is the energy barrier distribution of the pinning sites, while the DCD differentials, $\chi_{irr}^d(H)$, is the energy-barrier distribution associated with nucleation. Figure 47 illustrates the IRM and DCD differentials for the samples with 14 and 28 bilayers, respectively. The 14 bilayer sample showed a square loop, suggesting that $H_{DW} < H_N$, while the 28 bilayer sample showed a rounded loop indicative of $H_{DW} \ge H_N$.

5.1.2. Dy/Fe

As mentioned above, eq. (15) is only valid in the case of a broad and uniform distribution of energy barriers. If there is a narrow energy barrier or for small times, then other approaches must be taken to interpret the time-decay behavior. Kirby et al. (1991) studied the magnetization reversal through the Kerr rotation $\Theta_{\rm K}$ in 5 Å Dy/5 Å Fe and 5 Å Dy/4.5 Å Fe using a model originally developed by Fatuzzo (1962) for dielectric reversal in ferroelectrics. In this model, small reversed domains are presumed to nucleate at a constant rate, and then expand with constant domain wall velocity. Note that this approach is similar to the two-coercivity model present above. The Fatuzzo model predicts that the fractional area not yet reversed has the form

$$A(t) = \exp[-2k^2 + 2k^2Rt + 2K - (kRt)^2 - 2kRt - Rt + 2k^2(1 - k^{-1})\exp(-Rt)].$$
(17)

Here, R is the rate of domain nucleation, and k is a parameter related to the average velocity of domain wall motion, with $k = V_w/R\gamma_c$ where V_w is the domain wall velocity and γ_c is the initial radius of the domains. The complex form of this expression arises because overlap of the expanding domains must be taken into account. It should also be noted that this model does not include effects due to the changing demagnetization field, which could be of considerable importance.

There are two limiting cases in eq. (17). If the nucleation rate R is small and the domain wall velocity is large, then nucleation is an infrequent event, but once it occurs,



Fig. 48. Kerr rotation as a function of time for 5 Å Dy/5 Å Fe. The solid lines are the measured time dependence, while the dashed lines are nolinear least-squares fits to eq. (17). Different curves correspond to different reversing fields, with the uppermost curve corresponding to smallest field (after Kirby et al. 1991).

Fig. 49. Kerr rotation as a function of time after reversal for 5 Å Dy/4.5 Å Fe for several different values of the reversing field. The coercive field of this sample is 1.7 kOe (after Kirby et al. 1991).

the domains expand rapidly. This case is appropriate for 5 Å Dy/5 Å Fe. Figure 48 shows both the experimental decay curves (solid lines) and the fitting curves (dashed lines). The agreement is quite remarkable considering the simplicity of the model.

In the k=0 limit, magnetization reversal in the Fatuzzo model occurs only by nucleation, so that a purely exponential time decay is expected. The general form of the magnetization reversal data for 5 Å Dy/4.5 Å Fe (see fig. 49) suggests that it falls in this limit. However we find that the magnetization reversal data cannot be well fitted by the Fatuzzo model over a wide range in time. This is due likely to the combination of neglecting the change in the demagnetizing field during reversal and the presence of a distribution of nucleation rates. The latter effect of course is equivalent to a distribution of barrier heights to thermal activation. Both of these effects tend to lead to approximately $\ln(t)$ behavior at long times, as is observed experimentally. A model which can successfully describe the time decay behavior in both figs. 48 and 49 is described below.

5.1.3. Magnetization reversal model

Kirby et al. (1994) developed a simple model which is particularly useful for describing magnetization reversal in amorphous magnetic materials and multilayers with strong perpendicular anisotropy. They assumed that magnetization reversal in the uniform thin film occurs locally by thermal activation over the anisotropy barrier. They divided the sample into identical small volumes (cells) V_c , assumed that reversal occurred by coherent rotation, and proposed that the energy of the *j*th volume could be written as

$$E_j = K_{\rm u} V_{\rm c} \sin^2 \Theta_j - M_{\rm s} V_{\rm c} (H_z + \widehat{H}_j) \cos \Theta_j + \frac{1}{6} \left(3 - \frac{1}{2} S'_j \cos \Theta_j\right) E_{\rm w}.$$
 (18)

The first term on the right is the anisotropy energy, where $K_{\rm u}$ is the uniaxial anisotropy constant and Θ_i the polar angle of the magnetization of the volume. The second term is the magnetostatic energy of the moments in volume V_c , where H_Z is the component of the applied field normal to the film, and H_i is the local demagnetizing field. These two terms alone can result in quasi-ln(t) behavior at long time, as has been shown by Lottis et al. (1991) and by Lyberatos et al. (1990). The third term, analogous to a "wall energy", takes into account the likelihood that it is easier to reverse a volume near one that has already been reversed. Here, $S'_i = \sum m_i$, where the sum is over nearest neighbors of cell *i* and $m_i = +1$ if the moment of cell *i* lies along +Z and $m_i = -1$ if the moment of cell i lies along -Z. E_w is a measure of the reduction in energy which occurs. The third term is positive as an isolated cell reverses, and thus it tends to inhibit nucleation of reversed domains. On the other hand, if some of the neighboring cells have already reversed, the third term will be reduced or even be made negative and tend to enhance the probability of reversal. If E_w is large, eq. (18) predicts that nucleation will be followed by a rapid expansion of the domain. Kirby et al. (1994) used the barrier heights derived from eq. (18) to carry out Monte Carlo calculations of magnetization reversal in Dy/Fe multilayers, and some of their results are summarized in figs. 50 and 51.

Simulated magnetization decay curves for a sample with $K_u = 1 \times 10^6 \text{ erg/cm}^3$ and $M_s = 90 \text{ emu/cm}^3$ are shown in fig. 50. The volumes were adjusted to keep the simulated coercivity near 7 kOe. The solid line shows a decay curve for $E_w = 8 \times 10^{-13}$ erg. The rate of decay is initially slow, but it increases rapidly. Reversal goes to completion in a smooth fashion. This type of decay curve is expected when reversal occurs by slow nucleation followed by rapid domain expansion, as was illustrated in the discussion of the Fatuzzo model earlier. In the simulations of Kirby et al. (1994), this behavior occurs because thermal activated reversal, when E_w is large, is much more probable for cells at the domain wall than for cells far from a wall. The dashed curve shows a decay curve is quite different from that for $E_w = 8 \times 10^{-13}$ erg. The slope of the decay curve decreases monotonically, and complete reversal would take an extremely long time. Indeed, the magnetization varies approximately as $\ln(t)$ at long time. In this case,



Fig. 50. Simulated magnetization reversal curves for $E_w = 2 \times 10^{-13}$ erg (dashed line) and $E_w = 8 \times 10^{-13}$ erg (solid line) at room temperature. $V_c = 1.96 \times 10^{-18}$ and 1.70×10^{-18} cm³, respectively. $M_s = 90$ emu/cm³ and $K_u = 1 \times 10^6$ erg/cm³ for both curves. The inset shows the corresponding switching transitions at a field sweep rate of 200 Oe/s (after Kirby et al. 1994).



Fig. 51. Simulated reversed domain patterns at 30% reversal for the same two sets of parameters used to obtain fig. 50 (after Kirby et al. 1994).

the quasi-ln(t) behavior is due to the changing demagnetizing field as reversal occurs. Initially, the demagnetizing field serves to enhance the rate of reversal. As reversal occurs, the demagnetizing field reduces, and ultimately changes sign, so that it tends to inhibit further reversal. In the $E_w = 2 \times 10^{-13}$ erg case, the effects of the local demagnetizing field

tend to cancel the effects of the E_w term, so that there is only a small preference for reversal near already reversed calls. These points are illustrated in fig. 51. Figure 51a, for $E_w = 2 \times 10^{-13}$ erg, shows reversal primarily by nucleation, with little expansion of the domains once nucleated. Figure 51b shows the simulated domain pattern which occurs at 30% reversal for $E_w = 8 \times 10^{-13}$ erg. The domain structure in this case started with nucleation at a few random sites, with subsequent expansion of the domains. This model gives insights into the relationship between the macroscopic magnetic parameters and the reversal behavior and demonstrates the important role that thermal activation plays in the reversal process.

5.1.4. Micromagnetic calculations

The starting point for most micromagnetic calculations has been the Landau-Lifshiftz-Gilbert equation, which relates the time rate of change of angular momentum of the moments in the sample to the applied torque resulting from external magnetic fields and internal interactions (demagnetizing fields, anisotropy, and exchange). Usually a viscous damping term is also included. The micromagnetics approach is deterministic, in that coupled equations of motion are solved to follow the moment orientations as a function of time. While a detailed discussion of these techniques is beyond the scope of this review, we will summarize some of the results which have been obtained. It is important to note that such calculations require considerable computational power if they are to be carried out on a large scale, especially if long-range magnetic dipole interactions are to be properly included. For more details of the calculations, the reader is referred to the review article by Bertram and Zhu (1992) and a series of papers by Mansuripur and coworkers (Mansuripur 1987a,b, Mansuripur and McDaniel 1988, Mansuripur et al. 1991). It should be noted that these calculations are almost always equilibrium calculations carried out for T=0, and thus will not be directly comparable to experimental results at finite temperatures, where thermal activation can play an important role in the reversal process.

Mansuripur and McDaniel (1988) solved the Landau-Lifshitz-Gilbert equations for a two-dimensional square lattice of dipoles. They divided the thin film into $10 \text{ Å} \times 10 \text{ Å}$ cells and chose values of M_s and K_u appropriate for an a-R-T magneto-optic material. Assuming a perfectly anisotropic crystal (every cell has the same magnitude and direction for K_u), they start their simulations with an abrupt switch from up to down magnetization. They find that in zero applied field, the narrow wall relaxes to a finite width wall in times on the order of nanoseconds. When they apply an external field, they find that the wall moves with constant speed. To make the calculation more realistic they chose the *direction* of the local anisotropy in different cells to be randomly distributed. Their simulations for this case showed that Bloch lines appeared in the domain wall, and the presence of the random axis anisotropy led to a non-zero wall coercivity. Thus this approach may lead to detailed pictures of the nucleation energy and domain wall pinning mechanisms responsible for the coercivity at T=0.

In a more recent calculation, Mansuripur et al. (1991) and Giles and Mansuripur (1991) used simulations to investigate domain-wall coercivity on the submicron scale

in the presence of a variety of simulated defects and inhomogeneities. They found that in homogeneous samples the experimental nucleation fields were smaller than those necessary in the simulations, but if they introduced reversed magnetized seeds in regions of large local anisotropy, the experimental and simulated nucleation fields were brought much closer together. They mainly addressed the problem of wall coercivity in these materials, where the problem is that the simulated wall coercivity for homogeneous samples was smaller than the experimental values for homogeneous samples. In this case, they find that the inclusion of spatial fluctuations in the anisotropy and other structural and magnetic defects could *increase* the wall coercivity in the simulations. Thus it is suggested that the fluctuations in the local magnetic and structural parameters are responsible for many of the macroscopic magnetic properties of a-R–T materials.

5.2. Demagnetization anisotropy in CMF

The dipole-dipole contribution to anisotropy K_u in the macroscopic limit is known as the demagnetization anisotropy K_{de} . The value of K_{de} for a homogeneous film is $K_{de} = -2\pi M_s^2$ where M_s is the saturation magnetization. In multilayered films one normally use the same expression for K_{de} with M_s^2 replaced by its average value, $\langle M_s \rangle^2$. Kusov et al. (1992) derive the correct expression for the K_{de} valid for a multilayer film where the magnetization depends only on the Z coordinate. The derivation in the framework of a continuum approach gives

$$K_{\rm de} = -2\pi \left\langle M_{\rm s}^2 \right\rangle. \tag{19}$$

For a homogeneous film eq. (19) reduces to the standard form, i.e.

$$K_{\rm de} = -2\pi \left\langle M_{\rm s}^2 \right\rangle = -2\pi \left\langle M_{\rm s} \right\rangle^2$$

However, in a CMF structure with larger fluctuations of magnetization these two results are quite different. Assume that the magnetization may be expressed approximately as

$$M_{\rm s}(Z) = M_0 + \Delta M \sin\left(\frac{2\pi Z}{\lambda}\right),\tag{20}$$

where M_0 is the mean value of magnetization $M_s(Z)$, ΔM is the modulation amplitude and λ is the bilayer thickness. Then

$$K_{\rm de} = 2\pi \frac{1}{\lambda} \int_0^\lambda \left(M_0 + \Delta M \sin \frac{2\pi Z}{\lambda} \right)^2 \mathrm{d}Z = -2\pi M_0^2 \left(1 + \frac{\Delta M^2}{2M_0^2} \right). \tag{21}$$

One can see that the introduced error becomes large when ΔM is comparable with M_0 . Therefore one must use eq. (19) for calculating K_{de} to avoid error. The error introduced for multilayers with square-wave concentration distributions has also been discussed by Kusov et al. (1992).

5.3. Measurements of anisotropy and the R-T exchange coupling

The anisotropy of R-T alloys or R/T multilayers is usually measured with torque magnetometry (or VSM), Kerr effect, and extraordinary Hall effect. Wu et al. (1993) have done systematic measurements of K_u for $Tb_x(FeCo)_{1-x}$ alloys with different techniques and found that K_u measured by Hall effect and Kerr effect is always larger (by up to a factor of 3) than that from the torque techniques. The authors pointed out that the main difference among the techniques comes from the fact that different techniques measured torque is associated with the net magnetization of the R and T subnetworks; the Hall effect is contributed by the T subnetwork magnetization; and the Kerr effect is mainly contributed by the T subnetwork, but a small part of the signal also comes from the R subnetwork, depending on the laser wavelength. It is necessary to have a clear physical idea about the effects of measurement technique on the measured K_u value, and to interpret the magnetic behavior correctly.

The anisotropy behavior near the compensation point has received considerable attention for the R-T alloys and R/T multilayers. It is usually considered that the heavy R and T are coupled ferrimagnetically like a rigid body, i.e. the coupling strength Λ is infinity. Based on this assumption, the magnetic energy of a thin-film sample is written as (Hellman 1991):

$$E = -HM\cos(\alpha - \Theta) + (K_{\rm u} - 2\pi M^2)\sin\Theta, \qquad (22)$$

where Θ and α are the angles of M and H relative to the film normal. Minimizing E with respect to Θ for $\alpha = \pi/4$ gives an expression

$$\left(\frac{\tau}{H}\right)^2 = \frac{M^2}{2(K_{\rm u} - 2\pi M^2)}\tau + \frac{1}{2}M^2,\tag{23}$$

where $\tau = M \times H$ is the torque. Measuring τ as a function of H and then making a $(\tau/H)^2$ vs τ plot, one can find M and K_u simultaneously from the intercept and slope of the straight line passing through the experimental data. This analysis breaks down near the compensation point, where $M \approx 0$.

It appears from experiment that K_u drops for R–T alloys or R/T near the compensation point (Sato and Habu 1987, Shan and Sellmyer 1990b, Hellman 1991). This behavior was discussed by Hellman (1991) and Wu et al. (1993) in terms of a canting model, i.e. they considered the canting between the R and T subnetwork magnetizations, and the R–T coupling is not regarded as a rigid body.

In the canting model the magnetic energy of a thin film is (Hellman 1991)

$$E = \boldsymbol{H} \cdot \boldsymbol{M}_{\mathrm{R}} - \boldsymbol{H} \cdot \boldsymbol{M}_{\mathrm{T}} + \boldsymbol{\Lambda} \boldsymbol{M}_{\mathrm{T}} \cdot \boldsymbol{M}_{\mathrm{R}} + K_{\mathrm{u}} \sin^{2} \Theta_{\mathrm{R}} + 2\pi (M_{\mathrm{R}} \cos \Theta_{\mathrm{R}} - M_{\mathrm{T}} \cos \Theta_{\mathrm{T}})^{2},$$
(24)

where Λ is the coupling strength between R and T subnetworks, M_R and M_T are the magnetizations for R and T subnetworks, and Θ_R and Θ_T are the angles of M_R and M_T



Fig. 52. Schematic of magnetic field, subnetwork moments and their angles: (a) $M_R > M_T$, (b) $M_T > M_R$ (after Hellman 1991).

measured from the normal (fig. 52). Minimizing E with respect to Θ_R and Θ_T for $\alpha = \pi/4$ gives

$$\left(\frac{\tau}{H}\right) = (M_{\rm R} - M_{\rm T}) \frac{\sqrt{2}}{2} - \left(\frac{(M_{\rm R} - M_{\rm T})^2}{4K'_{\rm u}} + \frac{M_{\rm T}}{2M_{\rm R}\Lambda}\right) H,$$
(25)

where $K'_{\rm u} = K_{\rm u} - 2\pi (M_{\rm R} - M_{\rm T})^2$.

In the limit $\Lambda \rightarrow \infty$, values for the net magnetization $(M_R - M_T)$ and $K'_u = K_u - 2\pi (M_R - M_T)^2$ may be found from the intercept and slope of (τ/H) vs. H. These values are identical to those found in eq. (23). For finite Λ , however, the term $(M_T/2M_R\Lambda)$ in eq. (25) will cause an increased absolute value, and hence, if ignored, an artificially low value for K_u as $(M_R - M_T)$ is small. As $(M_R - M_T)$ approaches zero (i.e. near compensation), this term becomes increasingly large compared with $((M_R - M_T)^2/4K'_u)$, and hence K_u will appear to go zero at the compensation point. Also, as the real value of K_u increases, this reduction becomes significant at increasingly large values of $(M_R - M_T)$.

Wu et al. (1993) have studied the canting model in more detail and have given both the calculated and experimental data as shown in fig. 53 for $\text{Tb}_x(\text{FeCo})_{1-x}$ alloys with $A \approx 1800$. It is seen clearly that there is an anomalous drop near the compensation point when using torque magnetometry with the field at 45°. The figure also shows the experimental data and calculated K_u curve in terms of the extraordinary Hall effect. We notice that the torque technique produces a wider and deeper apparent dip and the Hall effect techniques produce a much narrower dip for the T-dominant case and a narrow peak for the R-dominant case.

The exchange-coupling strength Λ can be expressed and estimated as

$$\Lambda = \frac{2Z |J_{\rm R-T}|}{Ng_{\rm R}g_{\rm T}\mu_{\rm B}^2} \simeq 1800$$
(26)

for Tb(FeCo) with Z = 12, $J_{R-T} = -10^{-15}$ erg, $g_R = 1.5$, $g_T = 2$ and $N = 5 \times 10^{22}$ cm⁻³ (Wu et al. 1993). A may be determined experimentally in terms of the so-called "free-powder magnetization" approach which was analyzed in detail by Verhoef et al. (1990) and Zhao et al. (1993).


Fig. 53. Calculated K_u as a function of (M_R-M_T) . The solid line is the subnetwork (physical) anisotropy constant K_R . The dashed-dotted curve is for $K_u(45^\circ/T)$ i.e. K_u was measured by torque magnetometry with the field at 45°. The dashed and dotted curves correspond to $K_u(\text{Rot}/H)$ and $K_u(90^\circ/H)$, i.e. K_u was measured by Hall effect with rotating and in-plane field, respectively. The corresponding experimental data are also given (after Wu et al. 1993).

5.4. Orientation of magnetic moments in CMF

As discussed in sect. 3.3, the orientation of Fe-based R-T alloy or R/T CMF can be determined in terms of Mössbauer measurements. However, Wang and Kleemann (1991, 1992) proposed an analytical approach to determine the orientation of magnetic moments in Tb/Fe. As illustrated in fig. 54, Θ is the angle between the magnetic moment μ_i and the film normal Z, and δ is the angle between Z and the local easy axis \hat{n} . For multilayers, the total energies for the *i*th moment μ_i at the coordinate Z is expressed as

$$E_i(z) = -\mu_i(H + \bigwedge M)\cos\Theta - D'\cos^2(\delta - \Theta) - \mu_i H'\sin\Theta, \qquad (27)$$

where H is the applied field, \bigwedge is the mean-field coupling coefficient, D' is referred to the crystal-field coefficient (Wang and Kleemann 1991), and magnetization M is equal to $\mu_i Nm_i$, with N the number of moments per unit volume and

$$m_i = \langle \cos \Theta \rangle$$
 (28)

which accounts for the deviation of the local moment μ_i from the Z direction. In eq. (27), there are a Zeeman energy, an anisotropic exchange energy, a single-ion anisotropy energy



Fig. 54. Relative orientation of the atomic magnetic moment μ_i and the local easy axis *i* at the *i*th site. The applied field *H* is along the film normal *Z* direction and *H'* is the in-plane field (after Wang and Kleemann 1991).

and the energy induced by an in-plane field H'. H' is the field in the x-y plane which has to be accounted for owing to the existence of the in-plane magnetic vector in the pure Fe layers.

Classically the equilibrium position Θ of the moment is given by

$$\frac{\partial E_i(z)}{\partial \Theta} = \mu_i (H + \bigwedge M) \sin \Theta - D' \sin[2(\delta - \Theta)] - \mu_i H' \cos \Theta = 0.$$
⁽²⁹⁾

Then we obtain

$$\frac{\mu_i(H + \bigwedge M)}{D'}\sin\Theta - \frac{\mu_i H'}{D'}\cos\Theta = \sin[2(\delta - \Theta)]$$
(30)

or

$$\frac{(h+m_i)}{d}\sin\Theta - \frac{h'}{d}\cos\Theta = \sin[2(\delta-\Theta)],$$
(31)

where $d = D'/N \bigwedge \mu_i^2$ is the ratio of the energy of the single-ion anisotropy to the exchange energy $E_{ex} = N \bigwedge \mu_i^2$. $h = \mu_i H/N \bigwedge \mu_i^2$ is a reduced applied field and $h' = \mu_i H'/N \bigwedge \mu_i^2$ is a reduced field of H'. We let h' = 0.1 in the fitting procedure, because the in-plane field is much smaller than the exchange coupling and it appears reasonable from the fitting process. Following the treatment of Callen et al. (1977), where the reduced magnetization is taken as the spherical average,

$$m_i = \langle \cos \Theta \rangle = \frac{\int \cos \Theta \sin \delta \, \mathrm{d}\delta}{\int \sin \delta \, \mathrm{d}\delta},\tag{32}$$

assuming $0 \le \delta \le \pi/2$. We obtain the following expressions under the approximation of small and larger angle Θ ,

$$m_i \approx 1 - \left(\frac{4}{15} + \frac{3h'}{2}\right) d^2$$
 for small Θ , (33)

$$m_i \approx 0.5 + \frac{(1-h')}{6d}$$
 for larger Θ . (34)

From eqs. (34) and (35) we can see that there is a corresponding value of $m_i = \langle \cos \Theta \rangle$ for each value of d. As mentioned above, d is expressed as

$$d = \frac{D'}{N \bigwedge \mu_i^2} \tag{35}$$

Callen et al. (1977) pointed out that D' and \bigwedge can be determined by a fitting approach which is described in detail by Wang and Kleemann (1991). In sect. 4.1 the determination of magnetization distribution M(Z) has been discussed. If the applied field H is large enough to saturate magnetization, then

$$M(Z) = N\mu_i m_i = N\mu_i, \tag{36}$$

where $m_i = \langle \cos \Theta \rangle = 1$ because μ_i is along Z direction at saturated field. The conclusion is that μ_i is determined since M(Z) is known, $d = (D'/N \wedge \mu_i^2)$, and m_i is obtained from eq. (33) or (34), i.e. the orientation of μ_i at coordinate Z is obtained. Taking the average over the whole CMF along the Z direction, i.e.

$$\langle \cos \Theta \rangle = \frac{1}{\lambda} \int m \, \mathrm{d}z = \frac{1}{\lambda} \int \cos \Theta \, \mathrm{d}z,$$
 (37)

where λ is the bilayer thickness, the average orientation of $\langle \cos \Theta \rangle$ is found. Figure 55 shows the calculated result of $\langle \cos \Theta \rangle$ vs λ for Tb/Fe CMF. It shows strong PMA for $\lambda < 10$ Å, which agrees with the experiments fairly well.



Fig. 55. $(\cos \Theta)$ vs L in Tb/Fe multilayers obtained by fitting of experimental data. Inset: $(\cos \Theta)$ vs d according to eqs. (33), (34), where L is the bilayer thickness (Wang and Kleemann 1991).

138

6. Summary and conclusion

As stated at the outset, this review has focused on the fundamental aspects on which either (i) significant new understanding has emerged recently, or (ii) the level of understanding is so rudimentary that much work remains to be done. After thorough discussion through the above sections our understanding of the magnetic properties in R/T CMF has been improved in several ways. The interfacial magnetism is at the heart of the desired behavior such as large PMA and coercivity. Only the R/T CMF with nanoscale layer thickness may exhibit these properties because the interfacial magnetism dominates in this case. The interfaces can be regarded as compositionally modulated disordered R-T alloys, in which the composition and temperature dependences of magnetization can be calculated in terms of the mean-field model. Therefore the systematic studies of experimental results for layer thickness and temperature dependences of magnetization for R/T CMF can be understood. The interfacial magnetism is controlled by the interactions among R and T atoms and the local atomic arrangement or the structural anisotropy of constituent atoms. The layered or compositionally modulated structure in R/T offers an extra degree of freedom to control the local atomic arrangement and in consequence to tailor the CMF's magnetic properties. For the interactions among R and T atoms, we have seen that our understanding is limited to those situations where either random magnetic anisotropy or exchange fluctuations seem to operate nearly exclusively. Mean-field models of the two-subnetwork magnetic alloy are about the only available means of parameterizing the properties as a function of composition and temperature. Such models, for the most part, ignore local environment effects which are known to be important in certain cases where the T moments are unstable. Basic aspects of the phase transitions in the presence of both random anisotropy and exchange fluctuations are largely unexplored.

Our understanding of the origins of perpendicular magnetic anisotropy in a-R-T films has seen significant improvement recently. There has been a tendency in this field *to speak imprecisely about different mechanisms* which are not comparable, for example, in contrasting "pair ordering" with "single-ion" sources. It should be strongly emphasized that an understanding of PMA must include *both* (i) *the nature of the anisotropic atomic arrangements, and* (ii) *the fundamental physical interactions* which render the energy of one direction of magnetization lower than the other. In the case of a-R/T containing R atoms with orbital angular momentum, it now seems clear that growth-induced anisotropic pair correlations plus single-ion interactions caused by electric field gradients due to the non-isotropic R environments are the major sources of PMA. It has been shown that the anisotropic pair correlations in the typical sputtering situation can be controlled and enhanced by multilayering with characteristic individual layer thicknesses of about two monolayers. To create large PMA, besides the sharp boundaries of interfaces, i.e. the large average of the compositional modulation, the large magnetization of R subnetwork and short range anisotropic structure are necessary conditions as well.

For those a-R-T films containing Gd or other S-state ions, usually the magnitude of the PMA is rather small if present at all. In such cases the structural anisotropy plus spin-orbit interactions involving the Gd- or T-subnetwork or dipole-dipole interactions are the source of the anisotropy. In certain cases of Gd–T films where the value of K_u has been measured to be fairly large, the nature of both the anisotropic structure and the interactions are not entirely clear. This remains a topic for further research.

It is essential to determine the micromagnetic structure and compositional profile in the interface region experimentally. So far the magnetization distribution including the net, R and T subnetwork magnetizations and the composition distribution were obtained only by fitting approach based on the modified mean-field model. The MCXD technique has element specificity and can be used to deduce both of R- and T-subnetwork magnetic moment distributions as has been done for the Co/Pt multilayer by Schütz et al. (1992). The EXAFS technique by which Harris et al. (1992, 1993) determined local arrangement of Tb and Fe atoms may be used to determine the composition profile of the interface region.

We have given a brief review of studies of the magnetization reversal in R/T CMFs. Early models such as those of Street and Woolley (1949) and Fatuzzo (1962) are still widely used, but they show some limitations. Recent simulational studies have shown how semiquantitative understanding can be obtained based on fundamental magnetic parameters such as M_s and K_u , plus a small number of other parameters which must be determined by fitting to experimental data. These parameters, including cell volume and a domain-wall energy, must in future work be related to the fundamental atomic properties such as magnetic moments, local anisotropy, structural defects, and fluctuations in these quantities. This work has shown the importance of thermally activated processes in the magnetization decay and reversal processes.

In this review we have dealt only peripherally with the magneto-optic properties of R/T films. In general, these properties are rather similar to those of corresponding amorphous R-T alloys, particularly in the interesting limit where the R/T films have perpendicular anisotropy. A detailed discussion of such properties has been given in a review by Sellmyer et al. (1994).

Acknowledgments

We are grateful for financial support to the National Science Foundation under grants DMR-9222976 and OSR-9255225, and to the Center for Materials Research and Analysis supported by the Nebraska Research Initiative. We thank our colleagues R.D. Kirby, J.X. Shen, D. Wang, Y.J. Wang, and S.S. Jaswal for their collaboration and informative discussions.

References

- Attenkofer, K., S. Stähler, M. Knülle, P. Fischer, G. Schütz, G. Wiesinger and B. Scholz, 1993, J. Appl. Phys. 73, 6910.
- Baczewski, C.T., M. Piecuch, J. Durand, G. Marchal

and P. Delcroix, 1989, Phys. Rev. B 40, 11237. Badía, F., M.A. Badry, X.X. Zhang, J. Tejada, R.A. Brand, B. Scholz and W. Keune, 1991, J. Appl. Phys. 70, 6206.

- Baudelet, F., E. Dartyge, A. Fontaine, C. Brouder, G. Krill, J.P. Kappler and M. Piecuch, 1991, Phys. Rev. B 43, 5857.
- Bertram, H.N., and J.G. Zhu, 1992, Solid State Phys. 46, 271.
- Callen, E., Y.J. Liu and J.R. Cullen, 1977, Phys. Rev. B 16, 263.
- Cherifi, K., C. Dufour, M. Piecuch, A. Bruson, Ph. Bauer, G. Marchal and Ph. Mangin, 1991, J. Magn. & Magn. Mater. 93, 609.
- Egami, T., C.D. Graham Jr, W. Dmowski, P. Zhou, P.J. Flanders, E.E. Marinero, H. Notrys and C. Robinson, 1987, IEEE Trans. Magn. MAG-23, 2269.
- Ertl, L., G. Endl and H. Hoffmann, 1992, J. Magn. & Magn. Mater. 113, 227.
- Fatuzzo, E., 1962, Phys. Rev. 127, 1999.
- Fu, H., M. Mansuripur and P. Meystre, 1991, Phys. Rev. Lett. 66, 1086.
- Giles, R.C., and M. Mansuripur, 1991, Comput. Phys. 4, 204.
- Harris, V.G., K.D. Aylesworth, B.N. Das, W.T. Elam and N.C. Koon, 1992, Phys. Rev. Lett. 69, 1939.
- Harris, V.G., W.T. Elam and N.C. Koon, 1993, Correlation of Magnetic Structural Anisotropy in Amorphous Tb-Fe via EXAPS, in: Proc. Magneto-Optical Int. Symp. '92, Tucson, J. Magn. Soc. Jpn. 17(Suppl. S1), 267-271.
- Hasegawa, R., 1975, J. Appl. Phys. 46, 5263.
- Hellman, F., 1991, Appl. Phys. Lett. 59, 2757.
- Hellman, F., and E.M. Gyorgy, 1992, Phys. Rev. Lett. 68, 1391.
- Hellman, F., R.B. van Dover, S. Nakahara and E.M. Gyorgy, 1989, Phys. Rev. B 39, 10591.
- Honda, S., M. Nawate, M. Yoshiyama and T. Kusuda, 1987, IEEE Trans. Magn. MAG-23, 2952.
- Honda, S., M. Ohtsu and T. Kusuda, 1991a, J. Appl. Phys. 70, 6209.
- Honda, S., T. Kimura, M. Nawte and T. Kusuda, 1991b, Crystalline ferrimagnet-spin glass-amorphous ferrimagnet phase transition in Tb/Fe multilayers, Proc. Magneto-Optical Recording Int. Symp. '91, Tokyo, Japan, J. Magn. Soc. Jpn. 15(Suppl. S1), 61–64.
- Jaswal, S.S., 1992, Phys. Rev. Lett. 68, 1440.
- Kirby, R.D., J.X. Shen, Z.S. Shan and D.J. Sellmyer, 1991, J. Appl. Phys. 70, 6200.
- Kirby, R.D., J.X. Shen, R.J. Hardy and D.J. Sellmyer, 1994, Phys. Rev. B 49, 10810.
- Kusov, A.A., S.S. Jaswal and Z.S. Shan, 1992, Phys. Rev. B 46, 3123.

- Lottis, D.K., R. White and E.D. Dahlberg, 1991, Phys. Rev. Lett. 67, 362.
- Lyberatos, A., R.W. Chantrell and A. Hoare, 1990, IEEE Trans. Magn. MAG-26, 222.
- Mansuripur, M., 1987a, J. Appl. Phys. 61, 1580.
- Mansuripur, M., 1987b, J. Appl. Phys. 61, 3334.
- Mansuripur, M., and T.W. McDaniel, 1988, J. Appl. Phys. 63, 3831.
- Mansuripur, M., R.C. Giles and G. Patterson, 1991, J. Mag. Soc. Jpn. 15, 17.
- Mibu, K., N. Hosoito and T. Shinjo, 1989, J. Phys. Soc. Jap. 58, 2916.
- Mibu, K., N. Hosoito and T. Shinjo, 1993, A systematic study of magnetic anisotropy in Fe/rare-earth multilayers, Proc. Magneto-Optical Recording Int. Symp. '92, Tucson, AZ, USA, J. Mag. Soc. Jpn. 17(Suppl. S1), 38–39.
- Mizoguchi, T., and G.S. Cargill III, 1979, J. Appl. Phys. 50, 3570.
- Néel, M.L., 1954, J. Phys. Radium, 15, 225.
- O'Grady, K., V.G. Lewis and D.P.E. Dickson, 1993, J. Appl. Phys. 73, 5608.
- O'Grady, K., T. Thomson, S.J. Greaves and G. Bayreuther, 1994, J. Appl. Phys. **75**, 6849.
- O'Shea, M.J., S.G. Cornelison, Z.D. Chen and D.J. Sellmyer, 1983, Solid State Commun. 46, 313.
- Perera, P., and M.J. O'Shea, 1991, J. Appl. Phys. 70, 6212.
- Perera, P., M.J. O'Shea and A. Fert, 1991, J. Appl. Phys. 69, 5292.
- Sato, N., 1986, J. Appl. Phys. 59, 2514.
- Sato, N., and K. Habu, 1987, J. Appl. Phys. 61, 4287.
- Scholz, B., R.A. Brand, W. Keune, U. Kirschbaum, E.F. Wassermann, K. Mibu and T. Shinjo, 1991, J. Magn. & Magn. Mater., 93, 499.
- Schütz, G., H. Ebert, P. Fischer, S. Rüegg and W.B. Zeper, 1992, Spin Polarization of Pt in Pt/ Co Multilayers Studied by X-Ray Absorption, in: Mat. Res. Soc. Symp. Proc. 231, 77.
- Sellmyer, D.J., and S. Nafis, 1985, J. Appl. Phys. 57, 3584.
- Sellmyer, D.J., and M.J. O'Shea, 1983, J. Less-Common Met. 94, 59.
- Sellmyer, D.J., R.D. Kirby and S.S. Jaswal, 1994, in: The Magnetism of Amorphous Metals and Alloys, eds J. Fernandez-Baca and W.Y. Ching (World Scientific, Singapore).
- Shan, Z.S., and D.J. Sellmyer, 1990a, J. Appl. Phys. 67, 5713.
- Shan, Z.S., and D.J. Sellmyer, 1990b, Phys. Rev. B 42, 10433.

- Shan, Z.S., S. Nafis, K.D. Aylesworth and D.J. Sellmyer, 1988, J. Appl. Phys. 63, 3218.
- Shan, Z.S., D.J. Sellmyer, S.S. Jaswal, Y.J. Wang and J.X. Shen, 1989, Phys. Rev. Lett. 63, 449.
- Shan, Z.S., D.J. Sellmyer, S.S. Jaswal, Y.J. Wang and J.X. Shen, 1990, Phys. Rev. B 42, 10446.
- Shan, Z.S., B. Jacobsen, S.H. Liou and D.J. Sellmyer, 1991, J. Appl. Phys. 69, 5289.
- Shan, Z.S., J.X. Shen, R.D. Kirby and D.J. Sellmyer, 1994, J. Appl. Phys. 75, 6418.
- Shen, J.X., 1994, Ph.D. Dissertation (University of Nebraska).
- Shin, S.C., M.L. Cofied and R.H.D. Nuttall, 1987, J. Appl. Phys. 61, 4326.
- Street, R., and J.C. Woolley, 1949, Proc. Phys. Soc. London Sect. A 62, 562.
- Suzuki, Y., S. Takayama, F. Kirino and N. Ohta, 1987, IEEE Trans. Magn. MAG-23, 2275.
- van Dover, R.B., M. Hong, E.M. Gyorgy, J.F. Dillon Jr and S.D. Albston, 1985, J. Appl. Phys. 57, 3897.
- Verhoef, R., R.J. Radwański and J.J.M. Franse, 1990, J. Magn. & Magn. Mater. 89, 176.

- Wang, Y.J., and W. Kleemann, 1991, Phys. Rev. B 44, 5132.
- Wang, Y.J., and W. Kleemann, 1992, J. Magn. & Magn. Mater. 115, 9.
- Wu, T.-H., H. Fu, R.A. Hajjar, T. Suzuki and M. Mansuripur, 1993, J. Appl. Phys. 73, 1368.
- Wu, Y., J. Stohr, B.D. Hermsmeier, M.G. Samant and D. Weller, 1992, Phys. Rev. Lett. 69, 2307.
- Wybourne, B.G., 1966, Phys. Rev. 148, 317.
- Yamauchi, K., K. Habu and N. Sato, 1988, J. Appl. Phys. 64, 5748.
- Yan, X., M. Hirscher, T. Egami and E.E. Marinero, 1991, Phys. Rev. B 43, 9300.
- Yoden, K., N. Hosoito, K. Kawaguchi, K. Mibu and T. Shinjo, 1988, Jpn. J. Appl. Phys. 9, 1680.
- Zhang, H.Y., Y.J. Wang, G.G. Zheng, J.X. Shen, Z.S. Shan and D.J. Sellmyer, 1993, IEEE Trans. Magn. MAG-29, 3376.
- Zhao, Z.G., X. Li, J.H.V.J. Brabers, P.F. de Châtel, F.R. de Boer and K.H.J. Buschow, 1993, J. Magn. & Magn. Mater. **123**, 74.

Handbook on the Physics and Chemistry of Rare Earths Vol. 22 edited by K.A. Gschneidner, Jr. and L. Eyring © 1996 Elsevier Science B.V. All rights reserved

Chapter 149

THE ThMn₁₂-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES: STRUCTURE, MAGNETIC AND RELATED PROPERTIES

Wojciech SUSKI

W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 937, 50-950 Wrocław 2, Poland and International Laboratory of High Magnetic Fields and Low Temperatures, 95 Gajowicka Str., 53-529 Wrocław, Poland

Contents

	List of symbols and abbreviations	144
1.	Introduction	145
2.	ThMn ₁₂ -type structure	151
3.	Magnetic properties	157
	3.1. $(R, An)M_{12}$ -type compounds	158
	3.1.1. Compounds with $M = Mn$	158
	3.1.2. Compounds with $M = Fe$	160
	3.1.3. Compounds with $M = Zn$	160
	3.2. (R, An) $T_r M_{12-r}$ -type compounds	162
	3.2.1. Aluminides	162
	3.2.1.1. (R, An) M_4 Al ₈ -type	
	compounds	163
	3.2.1.1.1. M = Cr compounds	163
	3.2.1.1.2. M = Mn compounds	163
	3.2.1.1.3. M = Fe compounds	169
	3.2.1.1.4. M = Cu compounds	178
	3.2.1.2. (R, An)Fe ₅ Al ₇ -type	
	compounds	185
	3.2.1.3. (R, An) M_6Al_6 -type	
	compounds	190
	3.2.1.3.1. M = Cr compounds	190
	3.2.1.3.2. M = Mn compounds	190
	3.2.1.3.3. M = Fe compounds	190
	3.2.1.3.4. M = Cu compounds	195
	3.2.1.3.5. The aluminides with	
	other elements	195
	3.2.1.4. (R, An)Fe _x Al _{12-x} solid	
	solutions	195
	3.2.2. Gallides	202

3.3.	Compounds of the rare earths with high					
	concer	ntration of transition elements	206			
	3.3.1.	Bulk magnetic properties of the				
		rare-earth compounds	207			
		3.3.1.1. Compounds with Si	207			
		3.3.1.2. Compounds with Ti	210			
		3.3.1.3. Compounds with V	222			
		3.3.1.4. Compounds with Cr	233			
		3.3.1.5. Compounds with Mn	233			
		3.3.1.6. Compounds with Mo	233			
		3.3.1.7. Compounds with W	240			
		3.3.1.8. Compounds with Re	240			
	3.3.2.	Anisotropy	243			
	3.3.3.	Spin reorientation transition				
		(SRT)	247			
	3.3.4.	Theoretical considerations	252			
	3.3.5.	Improvement of magnetic				
		parameters	261			
		3.3.5.1. Admixture	261			
		3.3.5.2. Technological processes	264			
3.4.	Magn	etic properties of actinide				
	compo	ounds with high content of				
	transit	tion element	267			
	3.4.1.	Pure ternary compounds	267			
		3.4.1.1. $UFe_{10}Si_2$	267			
		3.4.1.2. UCo ₁₀ Si ₂	271			
		3.4.1.3. $UNi_{10}Si_2$	272			
		3.4.1.4. UFe ₁₀ Mo ₂	272			
		3.4.1.5. $UFe_{10}Re_2$	273			

W. SUSKI

	3.5. Pseudoternary alloys	274	Acknowledgements	286
4.	Conclusion	285	References	287

List of symbols and abbreviations

AF	antiferromagnetism,	\mathcal{H}_{CEF}	Hamiltonian describing CEF effect
<i>A</i> ^{<i>m</i>}	crystal-field potentials	\mathcal{H}_{ex}	Hamiltonian describing the exchange interactions
ASA	atomic sphere approximation	\mathcal{H}_{-}	Hamiltonian describing molecular
B	crystal-field parameters	· •m	field (MF) interactions
<i>B</i> ,	remanence	INS	inelastic neutron scattering
$(BH)_{max}$	maximal energy product	J	total angular momentum
C	specific heat	J_{R-Fc}	R-Fe coupling parameter
CAF	canted antiferromagnetic	J_{R-M}	exchange integral between R and M
CEF	crystalline electric field	j−j	intermediate coupling
CW, C–W	Curie-Weiss	$j_i(x)$	Bessel function
D	diamagnetism, diamagnetic	k _B	Boltzmann constant
d	average distance of nearest neighbors	K _i	anisotropy constant
DOS	density of states	L	orbital angular momentum
E_{A}, E_{a}	anisotropy energy	LHe	liquid helium (temperature)
E_a^0	energy of resonance without	LMTO	linear-muffin-tin-orbital (method)
-	exchange	LN_2	liquid nitrogen (temperature)
$E_{\rm DW}$	energy of domain walls	LRO	long-range order
E _{R,T}	free energy of rare earth (R) or	LSD	local spin density (approximation)
	transition metal (T) sublattices	LT	low temperature
E	parallel anisotropy energy	MM	magnetization
E_{\perp}	perpendicular anisotropy energy	MCW	modified Curie-Weiss
F	ferromagnetism, ferromagnetic	ME	Mössbauer effect
FC	field cooled	MF	molecular field
Fi	ferrimagnetism, ferrimagnetic	MFA	molecular field approximation (mean
FOMP	first-order magnetization process		field approximation)
FMR	ferromagnetic resonance	MV	mixed valence
fu	formula unit	MVM	magnetic valence model
g, g _j	Landé factor	$M_{\rm s}$	saturation magnetization
$g_{J}\mu_{B}\hat{J}\hat{J}$	interaction of R spin moment with molecular field, \mathcal{H}_m (MF)	M_{\perp}	magnetization perpendicular to easy axis
HF	heavy fermion(s)	M_{\parallel}	magnetization parallel to easy axis
НТ	high temperature	ND	neutron diffraction
$H_{\rm A}, H_{\rm a}$	anisotropy field	NMR	nuclear magnetic resonance
H_{c}	coercivity field	nn	nearest neighbor
H _{CR}	critical field	nnn	next-nearest neighbor
$H_{ m hf}$	hyperfine field	N _d	number of d electrons
\mathcal{H}_{m}	molecular field (MF)	$n_1(x)$	Neumann function
H _r	remanence	Р	paramagnetism, paramagnetic
${\cal H}$	total Hamiltonian	PCM	point charge model

144

$p_{ m eff}$	effective magnetic moment	U _x	exchange interactions for each pair of
p_0	ordered magnetic moment determined		d electrons of the same spin on the
	in ME or ND experiments		same atom
<i>p</i> _s	saturation magnetic moment	v, V	volume of chemical cell
$P(\theta)$	distribution function	WF	weak ferromagnetism
RKKY	Ruderman–Kittel–Kasuya–Yosida	W _d	bandwidth
	(interactions)	XPS	X-ray photoemission
RS	Russel-Saunders coupling	XRD	X-ray diffraction
RT	room temperature	ZFC	zero-field cooled
$\langle r^n \rangle$	Hartree-Fock radial integrals	Ζ	number of valence electrons
S	intrinsic (spin) angular momentum	Z_1	number of M neighbors of the
SC	superconductivity, superconductor		R atom
s.c.	single crystal	Z_2	number of next-nearest neighbors
SF	spin fluctuation	$Z(\theta, T)$	partition function
SG	spin glass	$Z_{\mathfrak{m}}$	magnetic valence
SPD	singular point detection (method)	$\langle Z_{ m m} \rangle$	average magnetic valence
SRO	short-range order	$\alpha(T)$	thermal expansion
SRT	spin reorientation temperature	β	critical exponent
	(transition)	Г	resonance width
S _M	spin of M atom	γ	coefficient of electronic specific heat
Т	temperature	$\varepsilon_{\rm d}$	Hartree-Fock energy of the atomic
$T_{\rm C}$	Curie point		d state
T _f	temperature of frustration	Θ	paramagnetic Curie temperature,
T _m	high-temperature magnetic phase		Weiss constant
	transition temperature	Θ_{D}	Debye temperature
T _N	Néel point	θ_n^m	Stevens factors ($\alpha_{\rm J}$, $\beta_{\rm J}$, $\gamma_{\rm J}$ for $n=2,4$
T_0	temperature separating two regions at		and 6, respectively)
	which a Curie–Weiss law is followed	$\mu_{ m B}$	Bohr magneton
_	with different p_{eff} and θ values	v	valence
T _{OG}	transition temperature from the	ρ	electric resistivity
T	aligned to random SG state	$ ho_{ m s}$	spin disorder resistivity
T _{SG}	temperature of the SG state formation	σ	specific magnetization
T _{SR}	spin reorientation transition (temperature)	X	magnetic susceptibility
TIP	temperature-independent		
	paramagnetism		

1. Introduction

The ThMn₁₂-type of tetragonal structure was described for the first time by Florio et al. (1952). However, it turned out that the binary compounds MM'_2 of the f-electron elements exist for only a few metals as the second component, i.e. Mn (Wang and Gilfrich 1966, Kirchmayr 1969, Deportes et al. 1977, Okamoto et al. 1987) or Zn (where M = Sm-Lu) (Iandelli and Palenzona 1967, Stewart and Coles 1974). In turn, as far as we know only

 $SmFe_{12}$ has been synthesized in the form of thin films (Hegde et al. 1991). MBe₁₂-type compounds are also known but in this case M represents only the 3d metals: Ti–Co.

In the study of the formation of ternary rare-earth compounds Zarechnyuk and Kripyakevich (1963) showed that for the Th Mn_{12} -type of structure the occurrence of a third component has a strongly stabilizing effect, extending this family enormously.

There are two distinct subgroups in this family of compounds: (1) those with a relatively low content of transition element, (2) those with a high concentration of the iron-group elements, mostly Fe, Co and Ni. For the first subgroup, the transition elements belong to the iron group except for Co and Ni, and the most popular stabilizing element is Al; however, Ga can also be used as a stabilizing component (Gladyshevsky et al. 1990, Weitzer et al. 1990, Burzo et al. 1992), or In (Sysa et al. 1989). Indium enters into $LnAg_{5.4}In_{6.6}$ systems, too (Sysa 1991). Ga stabilizes the ternaries with the same transition elements as Al, and additionally ThMn₁₂-type phases were found in the Dy–Co–Ga and Yb–Co–Ga systems (see Gladyshevsky et al. 1990). Contrary to other gallides, those with Co are reported to exhibit strictly limited compositions. For the actinides, only compounds with Al were found.

For the second subgroup, Si, Ti, V, Cr, Mn, Mo and Re are most frequently found as the stabilizing component for the rare-earth compounds, whereas only compounds with Si, and exceptionally with Mo and Re, are formed by uranium. The alloys of other actinides have not yet been obtained.

The phase equilibria in the ternary systems in which the ThMn₁₂-type structure is observed, were studied for numerous aluminides (see Gladyshevsky et al. 1990, Stelmakhovich 1991, Kuz'ma et al. 1992, Stelmakhovich et al. 1993) and for gallides (see Gladyshevsky et al. 1990). Also the equilibria in the many systems with higher content of the iron group elements were examined, e.g. Ce–Co–Mn, Ce–Fe–Mn, Ce– Fe–Mo, Ce–Fe–Re (see Gladyshevsky et al. 1990), Nd–Fe–Mo (Müller 1988), Sm–Fe–Ti (Neiva et al. 1991), Ln–Fe–(Co, Mo) (Müller 1988) and Ln–Fe–Ti (Sakurada et al. 1992), and numerous Y systems (Gladyshevsky et al. 1990). One can notice that the ThMn₁₂type phase is one of the most frequently observed in the R–M–M' systems.

Figures 1 and 2 show the Nd–Cu–Al (Zarechnyuk et al. 1975) and Nd–Fe–Mo (Müller 1988) systems, respectively, as examples of the phase relationships in the aluminides and alloys with higher Fe content. In both cases the Nd alloys are presented, because one hopes that this element exhibits some similarity to uranium and that therefore the conclusions concerning these systems can be extended to the uranium alloys. It follows from fig. 1 that the closest neighbors of the NdCu₄Al₈ phase are the Th₂Zn₁₇ and BaAl₄-type ternaries and some binary phases, and the ThMn₁₂ phase has a narrow range of existence. The same situation as concerns the neighborhood is true for the Pr–Cu–Al system, however, the ThMn₁₂ phase exists over a broader composition range: PrCu_{2.6–4}Al_{9.4–8} (Zarechnyuk and Rykhal 1978). The existence range is variable in different ternaries and we return to this problem in discussing the crystal structure. The majority of gallides exists in a broad range.

As mentioned above, figure 2 shows the iron-rich corner of the Nd–Fe–Mo system (Müller 1988). The closest neighbor of the Th Mn_{12} phase is the Th $_2Zn_{17}$ -type phase in this



Fig. 1. The aluminum-rich corner of the Nd-Cu-Al ternary system at room temperature (Zarechnyuk et al. 1975).

Fig. 2. The iron-rich corner of the Nd-Fe-Mo ternary system (Müller 1988).

system and also the Th₂Ni₁₇-type phase in other systems (see Gladyshevsky et al. 1990), whereas the study of the Sm-Fe-Ti system (Neiva et al. 1991) revealed 1:9 TbCu₇-type structure/Sm(Fe, Ti)₉ phase and 2:17 Th₂Zn₁₇-type structure/Sm₂Fe₁₇ phase. Therefore, one can expect these phases to be found as impurities in technological processes. The above considerations do not cover all the possibilities; e.g., magnetic investigations of $Ce_{10}Fe_{66}Mo_{24}$ (Berezyuk et al. 1994) suggest that $Ce_{1-x}Fe_x$ exists in this compound as an impurity.

W. SUSKI

As mentioned above, the first crystallographic investigations of the aluminides with lower concentration of transition element has been reported by Zarechnyuk and Kripyakevich (1963); this research has been followed up in the seventies (Buschow et al. 1976, van der Kraan and Buschow 1977, Buschow and van der Kraan 1978, Felner and Nowik 1978, 1979, Felner 1980), and magnetic examinations were then started almost simultaneously (see e.g. van der Kraan and Buschow 1977, Buschow 1977, Buschow and van der Kraan 1978, Felner and Nowik 1978, 1979). The same research on the materials with higher iron concentration was begun intensively much later, in the late eighties, motivated by the search for hard magnetic materials (de Mooij and Buschow 1987, Ohashi et al. 1987). Some results suggested potential application, e.g. a high Curie point and a high magnetization. The general disadvantage of these materials is their relatively low remanence. Some information had been available earlier, but in sources with narrower circulation (Yang 1981, Berezyuk et al. 1986).

The investigation of structure and physical properties of the actinide compounds with aluminum has been initiated in the eighties (Baran et al. 1984). In fact, the first examination of $ThFe_4Al_8$ was performed in 1978 (Buschow and van der Kraan 1978) but it has had an incidental character in the whole series of the lanthanide compounds. The actinide compounds with higher concentration of transition metals are under intensive examination since the end of the eighties (see e.g. Suski et al. 1989).

Paramount information on structure and phase equilibria of the ThMn₁₂-type compounds was collected by Gladyshevsky et al. (1990), while the structure and magnetic properties have been reviewed several times for rare-earth aluminides (Nowik and Felner 1983), rare-earth and actinide aluminides (Suski 1985), actinide aluminides (Sechovsky and Havela 1988), intermetallics with higher content of the iron-group metals for the rare earths (Buschow 1991, H.-S. Li and Coey 1991), and uranium (Suski 1992).

The vast majority of these studies were performed on the polycrystalline samples, as single crystals are rarely available (see e.g. Chełkowski et al. 1991, Fujiwara et al. 1987, Andreev et al. 1988, B.-P. Hu et al. 1990, Andreev et al. 1990, Drzazga et al. 1994); some of them are useful only for X-ray examination (see Ohashi et al. 1988a, Stępień-Damm et al. 1984, Gonçalves et al. 1992, etc.).

In the present review, we are going to discuss the structure, magnetic and related properties of the $ThMn_{12}$ -type phases of the rare earths and actinides with the main goal to compare their behaviors.

However, the comparison is extremely difficult due to pronounced differences between the electronic structure of lanthanides and actinides, particularly the light actinides and the normal lanthanides. One should remember that the f electrons in lanthanides are nicely localized, and magnetic ordering results from exchange interactions mediated by the RKKY interactions. Their interactions with the 3d electrons are set up according to clear-cut regulations, namely the total magnetic moment according to Hund's rules is a difference between or sum of the spin and orbital part for light and heavy lanthanides, respectively, and J is a good quantum number. Then the total lanthanide moment couples parallel to the 3d-metal magnetic moment for light lanthanides and antiparallel for heavy ones. The coupling is mediated by the orbital part. Sometimes the lanthanide magnetic moment is

Compound	$M_{s}~(\mu_{ m B}/{ m fu})$	$p_{\rm Fe}$ ($\mu_{\rm B}$ /Fe atom)	
YFe _{10.8} Ti _{1.2}	19.12	1.77	
YFe _{10.8} W _{1.2}	20.82	1.93	
YFe ₁₀ Cr ₂	16.67	1.67	
$YFe_{10.4}V_{1.6}$	17.93	1.72	
YFe ₁₀ V ₂	16.15 17.3 ^b	1.61	
YFe _{8.5} V _{3.5}	9.64	1.13	
GdFe _{10.8} Ti _{1.2}	13.36	1.88	
GdFe _{10.8} W _{1.2}	15.32	2.07	
GdFe ₁₀ Mo ₂	9.79	1.68	

Table 1 The saturation magnetization M_s and magnetic moment of the iron sublattice p_{fe}^{a}

^a Data from Verhoef et al. (1988).

^b Data from Helmholdt et al. (1988a).

lower than would follow from simple addition, usually due to crystal-field effects. For the ThMn₁₂-type compounds this scheme is experimentally confirmed when the concentration of iron-group element is high (see e.g. Haije et al. 1990, Helmholdt et al. 1988a, J. Hu et al. 1988). However, this is not true generally, and in GdMn₁₂ (Okamoto et al. 1987) the mutual orientation of magnetic moments of Gd and Mn is complex (see fig. 9, below). The Gd moment along the $\langle 100 \rangle$ direction is parallel to the moments of the Mn atom located in part on the 8(j) positions, referred to by authors as "D", and antiparallel to the moment of the Mn atoms located in part on the 8(i) positions, referred to as "A". Their "B" symbol corresponds to the Mn atoms located on the residual 8(i) and 8(j) sites having magnetic moments perpendicular to that of the Gd atoms and mutually antiparallel. The Mn atoms located on the 8(f) positions have very small magnetic moment. As mentioned above even in these compounds in which the magnetic moment of the lanthanide and iron sublattice are parallel or antiparallel their values do not correspond to the sum of magnetic-moment values. Table 1 lists the values of saturation magnetization and the iron magnetic moment estimated for Y and Gd compounds with various stabilizing elements and stoichiometry.

One can see that it is difficult to analyze the Fe sublattice moment listed in table 1. The moments evaluated for the Y compounds are supposed to be free from the influence of the magnetic lanthanides but the values are apparently strongly affected by the stabilizing element. The magnetic moments for the Y-Fe-V system for different concentrations, as presented in table 1, allow to estimate p_{Fe} for the hypothetical YFe₁₂, which amounts to 2.07 μ_{B} /Fe. Malozemoff et al. (1984) claimed that the difference between the magnetic moment of α -Fe (2.2 μ_{B}) and its binary alloys with nonmagnetic component T depends on the valence difference between Fe and T element. Results of Verhoef et al. (1988) prove that the same reasoning can be applied to the ternaries.

As concerns the light actinides (only the compounds of these elements with the $ThMn_{12}$ -type structure are known) the pronounced difference from lanthanide electronic

structure is obvious. The former elements develop a 5f-electron shell close to the Fermi surface, and the radius of the 5f-electron orbit is expanded and comparable to the radii of other outermost electronic orbits. For this reason, the 5f electrons are more sensitive to external factors than the 4f electrons and also enter into the interactions with band states. As a result, broadened 5f bands exist instead of discrete electronic levels. These bands are responsible for many unusual physical properties. Many phenomena follow from this behavior, e.g. heavy-fermion behavior, spin fluctuations, Kondo effect, hybridization, strong magnetocrystalline anisotropy, and complicated magnetic structures. Additional problems for the discussion of the electronic structure of the 5f-electron materials arise from the mutual ratio of the bandwidth and the magnitude of the spin–orbit coupling (Lander et al. 1991). For light actinides, the bandwidth is comparable with the L-S coupling and in individual cases this coupling can be broken so that the intermediate j-j coupling is observed. Therefore, coupling of the f electrons with 3d electrons mediated by the orbital part of the magnetic moment as in the case of lanthanides is excluded. Thus, one should look for another coupling mechanism (if any) in the 5f–3d materials.

In fact, the magnetic coupling for the ThMn₁₂-type compounds was determined only for the AnFe₄Al₈ series (see Gal et al. 1990) in a neutron diffraction (ND) experiment. Neutron investigations have been performed for other compounds as well, although for these either the transition-metal sublattice (Ptasiewicz-Bąk et al. 1988, Krimmel et al.1992) or both the actinide and transition-metal sublattices are nonmagnetic (Bourée-Vigneron et al. 1990). But this case is not interesting from the point of view of searching for rules on the 5f–3d coupling. If the coupling in AnFe₄Al₈ compounds corresponds to the scheme for light-lanthanide–transition-metal compounds the actinide sublattice should be coupled ferromagnetically to the transition-metal system. But that is not the case because the iron sublattice, 8(f), is antiferromagnetic; therefore some atoms are coupled ferromagnetically, and the others antiferromagnetically.

An additional complication is the possibility of spin-glass behavior which has been detected in these alloys.

As mentioned above, the extensive examination of the ThMn₁₂-type compounds of the lanthanides with a high concentration of transition element has been motivated by their uniaxial (tetragonal) structure being promising for anisotropy (which should be enhanced by the presence of the f-electron elements) or high magnetization and high Curie point (provided by a high concentration of iron or cobalt). One cannot expect, of course, any large-scale application of the actinide intermetallics; nevertheless, the high anisotropy of some of the uranium compounds ($K_1 = 10^{10} \text{ erg/cm}^3$ for US as reported by Lander et al. 1991; for reviews see Fournier and Troć 1985, Sechovsky and Havela 1988) suggested interesting behavior for this class of compounds and motivated us to start this type of research.

The majority of results for the ThMn₁₂-type compounds has been obtained from magnetometric, neutron diffraction and ⁵⁷Fe Mössbauer effect examinations, predominantly because of the iron sublattice. As far as we know there are only a few magneto-optical examinations (Brände et al. 1990, van Engelen and Buschow 1990, Beznosov et al. 1992), one ²⁹Si NMR study (Suski et al. 1993c), one high-resolution electron microscopy (Kępiński et al. 1994), one point charge spectroscopy examination (Naydyuk et al. 1993), and some X-ray spectroscopy experiments (e.g. Shcherba et al. 1992).

This chapter is organized as follows. After a short description of the $ThMn_{12}$ -type structure, the magnetic properties of the rare-earth and actinide compounds are discussed. These properties are determined by the methods mentioned above, and presented in sequence for the rare-earth and actinide aluminides and then for the compounds with higher concentration of the 3d metals. Some space will be devoted to the anisotropy and its sources in the investigated materials. There will be no discussion of interstitial pseudoternaries, because the huge amount of results there deserves a separate review. Next, the phenomenon of spin-rotation transition will be presented, followed by a short summary of theoretical problems: band structure and crystal-field interactions. Then, the technological processes applied for improving magnetic parameters will be reviewed. A special subsection will be devoted to the actinide compounds because of various main problems which are important for this family of compounds. Finally, a short résumé as well as some proposals for the further development of this research will be presented.

2. ThMn₁₂-type structure

The tetragonal ThMn₁₂-type of structure corresponds to the space group I4/mmm. This structure is presented in fig. 3. The 2(a) position is occupied by the f-electron element whereas in the 8(f), 8(i) and 8(j) positions other atoms are distributed. This distribution strongly depends on stoichiometry but also on the elements constituting the system. As far as magnetic properties are concerned special attention is due to the 8(i) position. The importance of this position was recognized for the first time by Melamud et al. (1987) who claimed that the 8(i) site is responsible for a "substantial" magnetic moment if occupied by the Fe atoms, whereas iron in the 8(f) and 8(j) sites does not carry a large moment. The cause of this behavior is that the Fe atom located in this position has the largest



Fig. 3. The Th Mn_{12} -type structure. See text for the distribution of the various kinds of atoms on the different sites.

W. SUSKI

				-	
Compound	R atom	<i>x</i> (i)	<i>x</i> (j)	Remarks	Ref.
UCr ₄ Al ₈		0.3444(4)	0.2816(4)	identified by ND	1
UMn ₄ Al ₈		0.3439(4)	0.2828(5)	identified by ND	1
UFe4Al8		0.34399(46)	0.28054(46)	identified by XRD	2
UCu _{4.25} Al _{7.75}		0.351(2)	0.282(3)	identified by ND at 1.6 K	3
$RFe_{10}V_2$	Nd	0.3634(4)	0.2722(2)	identified by ND at RT	4
$RFe_{10}V_2$	Tb	0.3613(6)	0.2755(4)	identified by ND at RT	4
$RFe_{10}V_2$	Dy	0.3612(8)	0.2781(4)	identified by ND at RT	4
$RFe_{10}V_2$	Ho	0.3627(6)	0.2765(4)	identified by ND at RT	4
$RFe_{10}V_2$	Er	0.3607(9)	0.2831(5)	identified by ND at 4.2 K	4
RFe ₁₀ V ₂	Y	0.3574(4)	0.2783(2)	identified by ND at 4.2 K	4

 Table 2

 x-coordinates at 8(i) and 8(j) at room temperature

References

(1) Bourée-Vigneron et al. (1990)

(2) Stępień-Damm et al. (1984)

(3) Krimmel et al. (1992)

(4) Haije et al. 1990

number of nearest-neighbor (nn) Fe atoms and the largest average Fe–Fe separation. This last statement concerns compounds with high Fe concentration. In the aluminides the transition elements occupy primarily the 8(f) position, whereas for compounds with larger concentration of the transition element the latter enters primarily the 8(j) and then the 8(i) positions.

Pearson (1984) noticed that the ThMn₁₂ structure contains two interpenetrating kagomé nets of Mn atoms that lie in the (100) and (010) planes. The nets are not planar since atoms located in the 8(i) and 8(j) positions have x-parameters of 0.275–0.284 (see table 2 for the uranium aluminides and the RFe₁₀V₂ compounds) instead of 0.250 for the ideal planar case.

Such arrangement results in interatomic distances that are generally shorter, or not much longer, than the appropriate atomic-radius sums. A compression of the atoms in the $ThMn_{12}$ structure compared with their elemental sizes is a condition that is common in the structures of most intermetallic phases.

Figure 4 presents the change of the crystallographic unit cell volume for the $(R, An)T_4Al_8$ -type compounds for different T elements (Buschow et al. 1976, Baran et al. 1987). This change is a monotonically decreasing function of increasing atomic number for actinides (only light ones); but for lanthanides the known lanthanide contraction has some exceptions, which is most pronounced for cerium compounds, and is probably due to the valence of cerium being different from 3+, as has been documented by X-ray spectroscopy experiments (Shcherba et al. 1992); table 3 lists the valence values.

The data presented in fig. 4 and table 3 are surprisingly in nice agreement. For cerium compounds the largest deviation from the 3+ valence is observed for the Fe compound which corresponds to the strongest deviation from a smooth curve for the unit cell volume,



Fig. 4. Unit cell volume for $(R, An)T_4AI_8$ ternaries (solid line, R, Buschow et al. 1976; dashed line, An, Baran et al. 1987).

Table 3 Valence of the (Ce, Yb)T₄Al₈ compounds^a

Compound	Valence	
CeMn₄Al ₈	3.18(5)	
CeFe ₄ Al ₈	3.28(5)	
CeCu ₄ Al ₈	3.00(5)	
YbCr ₄ Al ₈	mixed valence(?)	
YbFe ₄ Al ₈	3.00(5)	
YbCu ₄ Al ₈	2.47(5)	

^a Data from Shcherba et al. (1992).

but for the Cu compound the valence is 3 and there is no anomaly in fig. 4. For the Yb compounds a similar agreement is observed. Only the Fe compound does not exhibit such a nice correspondence because the small increase of the unit cell volume is not related to any valence deviation. Some space is devoted to the valence problem here because as far as we know this review is the only report dealing with that problem in the ThMn₁₂-type compounds. Buschow et al. (1976) have claimed that it does not make much difference whether one uses for R one of the (mostly trivalent) lanthanides or (tetravalent) thorium. However, at 1.8 Å the atomic radius of Th is close to those of the lanthanides and evidently, for creation of the ThMn₁₂-type of structure, size considerations are more important than the conduction-electron concentration or the relative difference in electronegativity between the components.

W. SUSKI

In the actinide aluminides a broad existence range has been reported for $UFe_{4+x}Al_{8-x}$ (Baran et al. 1985, Andreev et al. 1992a), $UCu_{4+x}Al_{8-x}$ (Geibel et al. 1990) and $UMn_{4+x}Al_{8-x}$ (Suski et al. 1995). However, information concerning the site occupation is available for copper compounds from neutron scattering (Krimmel et al. 1992) and for iron compounds from ⁵⁷Fe Mössbauer effect (ME) (Vagizov et al. 1995), and in these cases the excess Cu and Fe is substituted at the 8(j) sites. AnFe_{4+x}Al_{8-x} compounds additionally exhibit a deficiency in the Al sublattice, which seems to be the cause of additional complications in the magnetic properties of these materials; this will be discussed below (Gal et al. 1990).

As concerns the rare-earth compounds, according to Gladyshevsky et al. (1990), the broad range of existence was detected for the following aluminide systems: La-Mn-Al, Ce-Cr-Al, Pr-Cu-Al, Nd-Fe-Al, Sm-Fe-Al, Eu-Mn-Al, Dy-Fe-Al, Ho-Fe-Al and Er-Fe-Al. Recently, some other systems were reported to exhibit an existence range: Ho-Cu-Al (Stelmakhovich 1991), Yb-Cu-Al (Stelmakhovich et al. 1993) and Lu-Cu-Al (Kuz'ma et al. 1992). Neutron diffraction experiment showed that in the RFe₅Al₇ compounds with R = Tb, Ho, Er and Tm the excess Fe atoms enter the 8(j) positions (Kockelmann et al. 1994). The ⁵⁷Fe ME examinations show that for the RFe₆Al₆ compounds the 8(f) sites are occupied by the 8 Fe atoms, the 8(j) sites by the the 8 Al atoms and the remaining Fe and Al atoms enter the 8(i) sites statistically (Nowik and Felner 1983).

For the gallides, according to Gladyshevsky et al. (1990) existence ranges have been observed for the Y–Fe–Ga, Pr–Fe–Ga, Pr–Cu–Ga, Nd–Fe–Ga, Sm–Fe–Ga, Sm–Cu–Ga, Tb–Fe–Ga, Dy–Fe–Ga, Dy–Co–Ga, Ho–Fe–Ga, Ho–Cu–Ga, Er–Mn–Ga, Er–Fe–Ga, Tm–Fe–Ga and Yb–Fe–Ga systems. In some systems there exist compounds with a stoichiometry which is different from superstructure CeMn₄Al₈, but with a limited composition close to $RT_{5.5}Ga_{6.5}$ where R = Sm, Dy, Yb and Lu. Additionally, one should notice that gallides are formed also with Co, particularly, that with the special stoichiometry.

Figures 5–7 present the lattice parameters of the $RFe_{10}M_2$ compounds versus atomic number of the lanthanides or the ionic radius (fig. 5, Si: Buschow 1988a; fig. 6, Mo: Ermolenko et al. 1990; fig. 7, Re: Gueramian et al. 1991). For comparison, the lattice parameters of the respective uranium compounds are included (Suski et al. 1989, Gueramian et al. 1991). We do not know whether the U ion corresponds to $Pr(U^{4+})$ or to $Nd(U^{3+})$, so for the sake of the argument, following the precedent set in fig. 4, its compounds are located at the position of Nd. One can see that as a rule the lattice parameters of the uranium compounds are smaller than those of respective Nd or Pr compounds and this difference is more pronounced for *a*parameters. The difference probably results mainly from the smaller atomic radius of the uranium (1.38 Å). The observation is general, but one cannot discuss the absolute values because they strongly depend on the details of the preparation process and the small differences in stoichiometry. The lattice parameters presented in figs. 5–7 decrease monotonously with increasing of the atomic number in accord with the lanthanide contraction.



Fig. 5. Lattice parameters *a* (lower curve, left-hand scale) and *c* (upper curve, right-hand scale) for $\text{RFe}_{10}\text{Si}_2$ (Buschow 1988a). The parameters for UFe₁₀Si₂ are indicated by crosses (Suski et al. 1989).

Fig. 6. Lattice parameters *a* (lower panel) and *c* (upper panel) for RFe₁₀Mo₂ compounds (Ermolenko et al. 1990). The results for UFe₁₀Mo₂ were obtained by Suski et al. (1989).

The decrease of the *a*-parameters is stronger than that of the *c*-parameters, except for the Ce compounds, most probably resulting from the valence state of this element being different from 3. However, this is not generally true because J. Hu et al. (1988) reported for the RFe_{10.9}Ti_{1.1} series a pronounced minimum for the compound of Ho and strong increase for the Er compound. The authors do not propose any explanation of this anomaly.

The stoichiometry of the compounds with a high concentration of the 3d transition element does not necessary correspond to the $RM_{10}M'_2$ formula and a deviation is



Fig. 7. Lattice parameters a (upper curve) and c (lower curve) for RFe₁₀Re₂ compounds; the diamonds indicate the parameters for UFe₁₀Re₂ (Gueramian et al. 1991).

observed when M = Fe and M' = Ti (J. Hu et al. 1988), Mo and W (Buschow 1988a,b), V (Verhoef et al. 1988) and Re (Jurczyk 1990a); and for M = Co and M' = Ti (Solzi et al. 1988). It could be that the stoichiometry of these materials results from the broad existence range which was reported for many Y systems: Y-Fe-Ti (B.-P. Hu et al. 1989a), Y-Fe-V (Verhoef et al. 1988), Y-Fe-Cr (Buschow 1988a), Y-Fe-Mo and Y-Co-Mo (Gladyshevsky et al. 1990), and by Gladyshevsky et al. (1990) for numerous lanthanide systems: Ce-Fe-Mn, Ce-Co-Mn, Ce-Fe-Re, Ce-Mn-Ni, Pr-Co-Mn, Pr-Mn-Ni, Nd-Co-Mn, Nd-Mn-Ni, Sm-Co-Mn, Sm-Mn-Ni, Dy-Co-Re and R-Fe-Mo systems where R = Gd-Lu but not Yb alloys. Also the extended existence range has been reported by Andreev et al. (1991) for UFe_{12-x}Si_x where $1.3 \le x \le 3$.

As mentioned above for the $(R, An)M_{12-x}M'_x$ -type compounds, the R atom enters in principle into the 2(a) sites, and the other three sites are available for the M and M' atoms. The Fe, Co and Ni atoms, because of their large number in unit cell, occupy all types of sites, but there are strong preferences for the occupation of the remaining free sites. According to many authors the Mo, Ti, V and Cr atoms demonstrate the preference to enter the 8(i) sites, suggesting that the size effect does not substantially contribute in the formation of these compounds (de Mooij and Buschow 1988, Helmholdt et al. 1988a). The real mechanism for the distribution of the individual atoms is difficult to understand in terms of the formation enthalpies of R(Fe, M)₁₂ alone. An estimate of the relative enthalpies associated with the formation of a bond between the pairs of atoms involved can be obtained from the solution enthalpies. It follows from these data that, except for Si, the formation of the R–M bond is not advantageously energetic and therefore, the M atoms enter the sites which have a minimal contact with the R-sublattice 2(a) sites (Zarechnyuk and Kripyakevich 1963). This is confirmed by the occupation of the 8(f) and 8(j) and not 8(i) positions by the Si atoms in GdFe₁₀Si₂ (Dirken et al. 1989), in SmFe₁₀Si₂ (Buschow 1988a) and in UFe₁₀Si₂ (Berlureau et al. 1991); Si enters the 8(f) sites in UCo₁₀Si₂ (Berlureau et al. 1991) and the 8(j) sites in UNi₁₀Si₂ (Suski et al. 1993a). Finally, in YNi₁₀Si₂ (Moze et al. 1991) the Si atoms preferentially occupy the 8(f) sites, with some small occupancy also for both the 8(i) and 8(j) positions. However, in SmFe₁₁Ti the Ti atoms enter both the 8(i) and 8(j) sites (Ohashi et al. 1988b).

The statement about the rare-earth atoms exclusively occupying the 2(a) position is not true exactly: Bodak and coworkers reported some admixture of the lanthanide atom in other positions in the following systems: Ce–Co–Mn (Bodak et al. 1981), alloys of Fe and W with Ce, Pr, Nd and Sm (Bodak and Berezyuk 1983), alloys of Fe and Mo with the same lanthanides (Bodak and Berezyuk 1985), and the Dy–Fe–Re system (Sokolovskaya et al. 1985). Moreover, the Ce–Fe–Mo phase exists over a broad composition range of Fe and Mo, and the fraction of Ce entering other than 2(a) positions amounts to 0.025 (Bodak and Berezyuk 1985). This fraction is typical for other lanthanides and does not reach a value higher than 0.05. Unfortunately, the location of these excess lanthanide atoms has not been determined.

From the above discussion one can see that the $ThMn_{12}$ -type structure is complex, and it is impossible to formulate any clear-cut general rules of formation for the respective compounds. For the sake of simplicity pseudoternaries are omitted in the above considerations; some attention to their structure will be devoted in the description of their magnetic properties, for which the location of the individual components is of paramount importance.

3. Magnetic properties

In this section we present the magnetic and related properties of the various groups of the ThMn₁₂-type compounds (R, An)M₁₂ and (R, An)T_{12-x}M_x with 6 < x < 8 and with 1 < x < 3. Special attention will be devoted to improvement of magnetic parameters through substitution by other elements or, to lesser extent, by special preparation processes, to problems of anisotropy and their sources, spin-reorientation transitions, and the contribution of the f-electron atom to the magnetism of the compounds discussed. The influence of distribution of atoms over available crystallographic sites will be addressed mostly on the basis of Mössbauer-effect (ME) and neutron-diffraction (ND) measurements and occasionally X–ray diffraction (XRD). As mentioned above, the strong influence of the occupation of the 8(i) site by the Fe atoms (Melamud et al. 1987) is also considered in *ab initio* calculation of the magnetism of GdFe₁₂ by Trygg et al. (1992) who note that the 8(i) position has only one Fe atom at relatively close distance and 4 Fe atoms at a considerable larger distance. Due to this relative deficiency of close iron atoms, the associated magnetic moments become particularly large. However, this is not always true: neutron diffraction experiments performed on RFe₁₀V₂ compounds by Haije et al. (1990) show that the moment values of the 8(i) iron exceed those of the 8(j) and 8(f) iron atoms only in compounds in which R = Nd, Tb, Er or Y, but the iron moments at the 8(i) sites are substantially lower than those in the remaining sites in the compounds where R = Ho and Dy. The authors have no explanation for this nonsystematic variation of the iron moments.

3.1. $(R, An)M_{12}$ -type compounds

3.1.1. Compounds with M = Mn

Magnetic properties of binary M=Mn compounds are listed in table 4. They exist for heavier rare earths including Y and for Th. Preparation is difficult due to the high vapor pressure of Mn. For this reason the starting composition is usually $RMn_{12.5-13.0}$ and therefore the resultant alloys always contain some amount of the neighboring phases as impurities. After prolonged annealing these impurities are not observed by XRD.

Unfortunately, we could not find any magnetic data concerning $ThMn_{12}$. Attempts to obtain UMn_{12} turned out to be unsuccessful. The parameters presented in table 4 prove that AF-type magnetic ordering exists in the Mn sublattice below 87 K (Er) and

Compound	p_{s} (μ_{B})	T_C^{dc} (K)	T _C ^{ac} (K)	T _N (K)	$p_{ m eff} \ (\mu_{ m B})$	Θ (K)	Easy direct.	Remarks	Ref.
GdMn ₁₂	4.2ª	5.0	3.6	160	7.92	-80		⁵⁵ Mn NMR, peculiar magn. str.	1
	5.5	9.4(5) ^b						magn. struct.	4
								spin echo	3
				~120				electr. resist. vs. temperature	5
TbMn ₁₂	4.4	4.7	3.0	108	10.26	-7		⁵⁵ Mn NMR	1
	6.0	8.3(3) ^b						spin echo	3
							$\perp c$	magn. str.: Mn at 2 diff. magn. sites, Tb moment in basal plane	4 I
				~120				electr. resist. vs. temperature	5
DyMn ₁₂	5.05	2.2		100	10.25	-11		⁵⁵ Mn NMR	1
							$\perp c$		4
HoMn ₁₂	6.4	1.7		90	10.4	-8		⁵⁵ Mn NMR	1
							c		4
ErMn ₁₂	6.5	1.9		87	9.8		c		4
YMn ₁₂	0.42°			120				a = 0.859 nm, $c = 0.479$ nm; ND: magn. str. fig. 8	2
Gd*	$f(\mathbf{x})$				7			$Gd_{1-x}Y_xMn_{12}$	3

Table	- 4		
Binary compounds of the	ThMn ₁₂ -type	with	Mn

* Variable composition; see Remarks column.

^b Arrott plot.

 $^{c} p_{0}$.

^a Magnetic moment canted from the *a*-axis by an angle of 56.6°.

References

(1) Okamoto et al. (1987)

(2) Deportes and Givord (1976)

(3) Amako et al. (1992)

(4) Deportes and Givord (1977)

(5) Amako et al. (1993)



Fig. 8. Magnetic structure of YMn_{12} determined using neutron diffraction by Deportes and Givord (1976). Y atoms at the 2(a) sites and Mn atoms at the 8(i) and 8(j) sites lie in the planes z = 0 (full circles) and z = 1/2 (dashed circles). Mn atoms on the 8(f) sites are located at z = 1/4 and z = 3/4.

160 K (Gd) as the lowest and highest T_N temperature, whereas for the compounds containing magnetic lanthanides, ferromagnetic ordering is observed in the sublattice of these elements below 10 K. This low temperature obviously stems from the strong dilution of the lanthanide atoms (1:12). The various values of T_N for the Mn sublattice in other compounds than YMn₁₂ indicate a strong influence of the lanthanide atoms on magnetic properties, most probably through the band structure, i.e. the transfer of the rare-earth conduction electrons to the 3d band.

The magnetic structure of the Mn sublattice determined by neutron diffraction in YMn_{12} by Deportes and Givord (1976) is presented in fig. 8. The Shubnikov group of the magnetic structure is I_p4/m' mm. As the mirror planes contain atoms of the magnetic group, a given magnetic moment must transform into itself through the associated mirror plane. Although the magnetic structure is not collinear, the arrangements of magnetic moments between first neighboring atoms are nearly collinear. The magnetic structure of GdMn₁₂ has been proposed on the basis of the magnetic and NMR measurements (see sect. 1). This structure is presented schematically in fig. 9 (Okamoto et al. 1987); it has been described in sect. 1 and shows that the coupling between the lanthanide and transition metals is not necessarily parallel. Additionally, we should note that the Gd moments cant from the *a*-axis by an angle of 56.6° in the *a*-c plane.

In a discussion of the influence of the magnetic lanthanide atom on electronic structure of the ThMn₁₂-type Amako et al. 1992 drew an interesting conclusion from the concentration dependence of the saturation magnetic moment in the $Gd_{1-x}Y_xMn_{12}$ system. They showed that the magnetic moment of Gd gets closer to the free-ion value $(7\mu_B)$ when the Gd is more diluted. At the same time the Néel point decreases from 160 K to 120 K for the Gd and Y compounds, respectively. This difference suggests that the Gd atom induces an additional positive magnetic interactions in the Mn sublattice whereas the other lanthanide atoms seem to induce negative interaction resulting in lower T_N .



Fig. 9. Magnetic structure of $GdMn_{12}$ proposed by Okamoto et al. (1987) on the basis of magnetic and ⁵⁵Mn NMR examination. Atoms located at 8(f) have negligible magnetic moment and are not shown.

The electric resistivity of YMn_{12} , $GdMn_{12}$ and $TbMn_{12}$ has been measured by Amako et al. (1993). The temperature dependence of the electric resistivity exhibits a Néel point about 120 K for all compounds with a remarkable anomaly below this temperature. It has been suggested that the anomaly is due to an AF band gap.

3.1.2. Compounds with M = Fe

Only the SmFe₁₂ binary compound has been synthesized (Hegde et al. 1991) as an oriented sputtered thin film with a slight iron deficiency. The crystallographic and magnetic data are listed in table 5. This film is strongly (002) textured and the anisotropy field is estimated to be about 13 T. Navarathna et al. (1992) have shown that the texturing can be switched from (002) to (200) and the SmFe₁₂ (222)-textured films could be synthesized with higher coercivities than (002)-textured films. For (222)-textured films the crystallite *c*-axes make an angle of 51° with respect to the film plane, versus 90° for (002)-textured films. Consequently, their hysteresis loop is less square for this texture than for an ideal (002)-textured films. The H_c values necessary to switch the texture direction, perpendicular and in-plane for the (222) sample, were 2.5 and 3.2 kOe, respectively.

GdFe₁₂ does not exist as a stable compound but electronic structure calculations using the LMTO–ASA method by Trygg et al. (1992) have been performed. As was observed in the experiment on the RMn_{12} systems there is a pronounced influence of localized 4f magnetism on the conduction-band magnetism (transition-metal sublattice) which gives noticeable changes in the local moment of the iron (transition element). The presence of the 4f spin moment is found to induce a redistribution of the spin moment between the rare-earth and iron sites, while the total conduction-electron moment remains constant. It seems that these conclusions have also some importance for the ternary materials.

3.1.3. Compounds with M = Zn

The lattice parameters and magnetic properties of compounds with M=Zn are listed in table 5. According to Iandelli and Palenzona (1967) only the compounds of the heavy lanthanides exist. Since the Zn sublattice is nonmagnetic the magnetic properties of these alloys are related exclusively to the lanthanide atoms. The lattice parameters reported by landelli and Palenzona (1967) follow the lanthanide contraction, however, the data of

		•	-			12 71		
Compound	<i>a</i> (nm)	с (nm)	Т ^{м а} (К)	T _N ^{E a} (K)	$p_{ m eff} \ (\mu_{ m B})$	Ө (K)	Remarks	Ref.
YFe ₁₂							⁵⁷ Fe ME, $H^{\rm hf} = 37.7 {\rm T}$	1
SmFe ₁₂	0.8438(5)	0.4805(5)					crystalline thin film, $p_s \approx 1.8\mu_{\rm B}/{\rm Fe}$ atom, $H_{\rm c} = 0.6 {\rm T}^{\rm b}$; c-axis perpendicular to the film plane	2
GdFe ₁₂							does not exist as a stable compound; <i>ab initio</i> calculation of magnetism	3
YZn ₁₂	0.8861	0.5205						4
SmZn ₁₂	0.8927	0.5215	15	14	0.74	-27.8		5,6°
GdZn ₁₂	0.8898	0.5210	16	15.25	8.40	-58		5,6°
TbZn ₁₂	0.8856	0.5199						4
	0.8884	0.5200	14	13	10.14	-38		5,6°
DyZn ₁₂	0.8872	0.5204						4
	0.8877	0.5198						6
HoZn ₁₂	0.8868	0.5195						6
ErZn ₁₂	0.8850	0.5195						4
	0.8863	0.5195	2.8	2.76	9.67	+3		5,6°
TmZn ₁₂	0.8863	0.5190	0	0				5,6°
YbZn ₁₂			0	0				5
LuZn ₁₂	0.8848	0.5186	0	0				5,6°

Table 5 Binary compounds of the Th Mn_{12} -type with Fe and Zn

^a T_N^M determined in magnetometric measurements; T_N^E determined in resistivity measurements.

^b For the onset of ferromagnetic order.

^c Lattice parameters.

References

(1) I	Denissen	et	al.	(1990)
-------	----------	----	-----	--------

(2) Hegde et al. (1991)

(3) Trygg et al. (1992)

(4) Kuz'ma et al. (1965)

(5) Stewart and Coles (1974)

(6) Iandelli and Palenzona (1967)

Kuz'ma et al. (1965) exhibit some irregularity for Dy and Er compounds. Contrary to the Mn compounds, magnetic order in the lanthanide sublattice has antiferromagnetic character. The Néel points determined in magnetic measurements are close to that obtained from examination of the resistivity by Stewart and Coles (1974). The magnetic susceptibility of these materials follows a Curie–Weiss law above 100 K and effective magnetic moment values are close to that expected for the trivalent lanthanide free ions. Because the AF ordering temperatures of the RZn_{12} compounds are low, the phonon resistivity is small compared to the spin-disorder resistivity, ρ_s , even at T_N . Therefore, the disorder contribution can be determined with good accuracy and the dependence of ρ_s



Fig. 10. Total spin disorder resistivity, ρ_s , versus $(g-1)^2 J(J+1)$; ρ_s has been corrected by a small phonon contribution at T_N (Stewart and Coles 1974).

on temperature T is $\rho_s \sim T^{1.38}$ for GdZn₁₂, $\rho_s \sim T^{1.45}$ for TbZn₁₂, $\rho_s \sim T^{5.9}$ for SmZn₁₂, and $\rho_s \sim T^{6.5}$ for ErZn₁₂ (Stewart and Coles 1974). These results cannot be related to any existing theories of electron-magnon scattering. In fig. 10 the total spin-disorder resistivity, ρ_s , normalized to that of GdZn₁₂ after correcting for the small phonon contribution at T_N , is presented versus $(g-1)^2 J(J+1)$, where g is the Landé factor and J is the angular momentum of the rare earth. The ρ_s values of Tb and Er compounds are smaller than expected from the linear plot. This might result from a non-S ground state. Specific-heat measurements (Stewart 1973) demonstrate that in ErZn₁₂ probably only one CEF doublet (the ground state) is involved in the magnetic transition. In turn, ρ_s for SmZn₁₂ is slightly larger than expected, suggesting a contribution other than exchange scattering.

3.2. (R, An) $T_x M_{12-x}$ -type compounds

3.2.1. Aluminides

The magnetic and some related properties of the ThMn₁₂-type aluminides will be presented below. The authors usually distinguish three types within these materials: (R, An)T_xAl_{12-x}, with x=4, 5 and 6. However, this is only a simplification for easier presentation of the results, and in reality solid solutions with $3 < x \le 6$ or sometimes even higher x were reported (see e.g. Kamimori et al. 1988, Zeleny et al. 1991). Nevertheless, we present in principle the results according to stoichiometry with x=4, 5 and 6. At the end of this subsection we will describe the systems which are explicitly determined as a solid solutions.

X-ray and ME investigations show that for the materials with x = 4 the transition metal occupies mostly the 8(f) crystallographic position, and with increasing x the 8(j) site is populated, sometimes exclusively as reported for the UCu_{4+x}Al_{8-x} system (Krimmel et al. 1992) or with a strong preference over the 8(i) position. It might be that in the case of T = Fe this discrimination of the 8(i) position is a reason for the relatively low Curie point, below about 300 K in these materials.

3.2.1.1. $(R, An)M_4Al_8$ -type compounds. These compounds form a kind of superstructure because the transition element enters exclusively the 8(f) position as has been shown in numerous ND and ME experiments. The results of different examinations are collected in tables 6 - 12 below.

3.2.1.1.1. M = Cr compounds. As follows from table 6 these compounds exhibit AF ordering with the exception of La, Ce, Nd, Yb, Lu, Y, Th and U compounds. The ordering exists only in the lanthanide sublattice, and that is the reason for the relatively low Néel points (below 20 K). Among the actinides, the magnetic ordering in NpCr₄Al_{8-x} is observed in the Np as well as Cr sublattices but the ordering temperatures are quite close (~55K) and cannot be distinguished (Gal et al. 1987). The angle between hyperfine field and c-axis observed in the ⁵⁵Gd Mössbauer experiment in $GdCr_4Al_8$ by Felner and Nowik (1979) suggests a possibility that the AF structure in these materials is not necessarily collinear. Also the temperature dependence of magnetization reported by Felner and Nowik (1979) is not typical for AF. In most of the compounds a sharp rise of the magnetization is clearly seen at low temperature. On the one hand the magnetic moments determined at 1.1 K under an applied field of 1.7T are low compared to their free-ion value. Only the temperature dependence of magnetization of GdCr₄Al₈ is typical for an antiferromagnet. On the other hand, the paramagnetic Curie temperatures Θ are negative for all magnetic RCr₄Al₈ type compounds, hence Felner and Nowik (1979) concluded that all these compounds order antiferromagnetically. The lack of magnetic order in the compounds of La, Ce, Lu, Y, Th and U is clear evidence that the Cr ions do not carry any localized magnetic moment. However, the enhanced Curie constants determined for magnetic compounds indicate that magnetic R ions induce small magnetic moment (about $0.1\mu_{\rm B}$) in the Cr sublattice. For SmCr₄Al₈ there is evidence of a contribution of the ionic excited states into the 6H_{5/2} ground state, and thus it is not justified to compare the results for this compound to the free-ion value for peff. The positive Curie-Weiss temperature as well as the value of the magnetic moment for YbCr₄Al₈ may suggest a mixed-valence state. ME provides evidence of ~10% admixture of Yb^{3+} in the predominantly Yb^{2+} (Felner and Nowik 1979). The mixed-valence state is also confirmed by unit cell volume results (Felner and Nowik 1979) and an X-ray spectroscopy experiment by Shcherba et al. (1992).

At present we do not know why UCr_4Al_8 does not follow the Curie–Weiss law (Baran et al. 1987). Magnetic order as the cause of this behavior is excluded by a neutron diffraction study (Bourée-Vigneron et al. 1990). Therefore, the cause could be a partial delocalization of the uranium 5f electrons.

3.2.1.1.2. M = Mn compounds. The results concerning magnetic and related properties of the (R, An)Mn₄Al₈-type compounds are collected in table 7. In these compounds only the lanthanide sublattice seems to order magnetically (AF) except for the compounds of La, Ce, Yb and Lu. The compounds of Y, Th and U are also nonmagnetic. This observation is strange because in the ThCr₂Si₂-type compounds the exchanges in the Mn sublattice are strong and magnetic order is observed above room temperature (see Szytuła 1991). It is, however, possible that in the compounds containing a magnetic Table 6 Ternary (R, An)Cr₄Al₈-type aluminides

	Ref.		1	2	1	2	1	2	3	1	7	7	7	1	2	2	4	7	1	Ŷ	2	7	1	3	3	1
) Remarks			⁵⁷ Fe ME					Ce valence state by X-ray spectroscopy						¹⁵⁵ Gd ME, angle between $H_{\rm hf}$ and c -axis	⁵⁷ Fe (admixt) ME	¹⁶¹ Dy ME			Nd:Cr 93% in 8f, 5% in 8j, 2% in 8i	¹⁶⁶ Er ME			Yb valence state by X-ray spectroscopy	¹⁷⁰ Yb ME, additional phase	
	p _{eff} (C1	$(\mu_{\rm B})$									0.16	0.12	0.61		0.15	0.08	0.12				0.08	0.07			0.1	
	p _{eff} (R)	$(\mu_{\rm B})$									3.58	3.62	0.86		7.94	9.72	10.63	10.6			9.59	7.57			1.45	
•••	θ	(K)									-16(2)	-11(2)	-24(2)		-9(2)	-5(2)	-5(2)	-5(2)			-4(2)	-11(2)			+7(2)	
	$H_{ m hf}$	Ð													10.2(5)		$-835(30)^{b}$				1790(5) ^b					
	p_0^{a}	$(\mu_{\rm B})$									0.38		0.03		1.5	3.5	4.2	4.1			3.8	2.4				
	$T_{\rm N}$	(K)									6(2)		19(2)		8(2)	12(2)	16(2)	8(2)			14(2)	11(2)				
	magn.	state									AF	Р	AF		AF	AF	AF	AF			AF	AF				
	0	(mn)	0.5122	0.5130	0.5137	0.5127	0.5131	0.5128		0.5128	0.5135	0.5136	0.5136	0.5128	0.5133	0.5130	0.5132	0.5126	0.5123	0.51244	0.5124	0.5131	0.5119		0.5132	0.5119
	а	(uuu)	0.9891	0.8920	0.9156	0.9131	0.9022	0.9042		0.9033	0.9023	0.9000	0.8973	0.8967	0.8950	0.8925	0.8926	0.8910	0.8967	0.89244	0.8903	0.8903	0.9011		0.8945	0.8884
	R/An		Y		La		లి			Pr		PN	Sm	Gd		Tb	Dy	Ю	Er			$\mathbf{T}_{\mathbf{m}}$	Υb			Lu

W. SUSKI

continued on next page

						Table 6,	continue	p			
R/An	a	c	magn.	$T_{\rm N}$	P_0^{a}	$H_{ m hf}$	θ	$p_{\mathrm{eff}}(\mathrm{R})$	p _{eff} (Cr)	Remarks	Ref.
	(uu)	(uu)	state	(K)	$(\mu_{\rm B})$	E	(K)	(<i>µ</i> ^B)	$(\mu_{\rm B})$		
L H	0.9012	0.5140								atomic position	1
	0.9011	0.5151	TIP								7
n	0.8907	0.5122								no CW behavior	9
	0.89132(4)	0.51091(3)	P۰							ND, atomic positions	4
Np*	0.893(1)	0.515(1)	AF	55(3	0	280(10)	+6.0			NdCr ₄ Al _{$8-x$} : ²³⁷ Np ME, magnetic order occurs on both Np and Cr sites with close ordering temperature	~
* Varić * At 4.	able composition 2 K.	on; see Remai	rks colum	u.			, In Dc	M c/s. wn to 1.4	45 K.		
<i>Refere</i> : (1) Bu (2) Fel (3) Sh (4) Bo	nces schow et al. (1 ner and Nowil cherba et al. (1 urée-Vigneron	976) c (1979) 992) et al. (1990)					(3) 1 $(6) 1$ $(7) 0$	Moze et a Baran et a Gal et al.	ul. (1990 al. (1987) (1987)	(a)	

continue
6, 6
ole

	Ref.	- 2	3	1	4	2	1	2	oscopy, $v = 3.18 = 5$	4		9	2	9	2	2	it state 2	-	$\operatorname{reen} \boldsymbol{H}_{\mathrm{hf}}$ and \boldsymbol{c} 2 7	continued on next page
) Remarks		MCW		$\alpha(T)$	additional phase			valence state by X-ray specti	L _{III} absorption edge		NDb		NDb			¹⁵¹ Eu ME; Eu in mixed vale		¹⁵⁵ Gd ME, 46(6)° angle betw ESR	
nides	$p_{\rm eff}({ m Mn})$ $(\mu_{ m B})$		3.93					0.9					1.6			1.4			1.6	
e alumir	$p_{\rm eff}({ m R})$ $(\mu_{ m B})$												3.58		3.62	0.86			7.94	
n₄Al _s -typ	θ (K)		1110					+8(2)					-1(2)		-8(2)	-18(2)			+4(2)	
nary (R, An)M	$_{ m (T)}^{H_{ m hf}}$																		10.2(5)	
2	${P_0}^{\mathrm{a}}$ (μ_{B})												2) 0.38		2) 0.48	2) 0.14	2) 0.46		2) 3.1	
	$\stackrel{T_{\mathrm{N}}}{(\mathrm{K})}$												11(7(12(20(28(
	magn. state												AF		AF	AF	AF		AF	
	c (nm)	0.5103 0.5101		0.5166	0.5167		0.5133	0.5150			0.5143	0.51459		0.51357	0.5133	0.5120	0.5161	0.5119	0.5116	
	a (nm)	0.8856 0.8857		0.9031	0.9057		0.8947	0.8910			0.8962	0.89617		0.89365	0.8925	0.8902	0.8982	0.8887	0.8911	
	R/An	۲ ۲		La			ပီ				Pr			PN		Sm	Eu	Gd		

w. suski

166

						Table '	7, continue	p			
R/An	a	c `	magn.	TN	P_0^a	H _h	0	p _{eff} (R) 1	و _{eff} (Mn)	Remarks	Ref.
	(uu)	(uu)	state	(k)	(<i>m</i> ^B)	(1)	(K)	$(\mu_{\rm B})$	(μ _B)		
Ъ	0.88680	0.51029								ND ^b	9
	0.8865	0.5108	AF	21(2)) 4.3	5.9(5)	+7(2)	9.72	1.7	⁵⁷ Fe ME, 48.56° angle between $H_{\rm hf}$ and c	7
										INS CEF parameters	×
Dy	0.88545	0.50991								NDb	9
	0.8849	0.5112	AF	19(2)) 4.0	-835(30)°	-26(2)	10.63	1.9	¹⁶¹ Dy ME	1
Но	0.88503	0.50968								ND ^b	9
	0.8845	0.5097	AF	14(2)) 4.8		-2(2)	10.6	1.5		7
										INS CEF parameters	×
Er	0.8829	0.5096									1
	0.8837	0.5093	AF	15(2)) 4.1	1735(5)°	-2(2)	9.59	1.0	¹⁶⁶ Er ME	7
Tm	0.8848	0.5080	AF	13(2)	3.7		+5(2)	7.57	1.5		7
Yb	0.8819	0.5084					,				1
	0.8875	0.5111									7
										$\alpha(T)$	4
Lu	0.8814	0.5083	ፈ				10(2)	0.9			7
Тћ	0.8937	0.5639									I
	0.8963	0.5150	MCW						0.4	$\chi_0 = 8.75 \times 10^{-3} \text{ g cm}^3 \text{ mol}$	6
n	0.8849	0.5104	ч							no CW behavior	6
	0.8845(3)	0.5096(1)	$\mathbf{P}^{\mathbf{q}}$							ND, atomic positions	10
^a At 4.	2K.						° In	M c/s.			
ն Mn 5	3% in 8(f), <u></u>	5% in 8(j) an	id 2% in 8	(j)			d Do	wn to 1.	45 K.		
Referen	ces										
(1) Busi	thow et al. (19'	76)			(5) Shche	srba et al. (1992)				(9) Baran et al. (1987)	
(2) Feln (3) Cold	er and Nowik (ea et al. (1994)	(1979) hì			(6) Moze (7) Colde	et al. (1990b) a et al. (1994a)				(10) Bourée-Vigneron et al. (1990)	
(4) Kote	rlin et al. (199	3 6			(8) Moze	et al. (1990a)					

lanthanide atom, the lanthanide element induces magnetic order in the Mn sublattice and the R and Mn sublattices order antiferromagnetically.

Coldea et al. (1994a,b) claim that the occurrence of a magnetic moment, at least in YMn₄Al₈ and GdMn₄Al₈ is strongly correlated with the critical value of the Mn-Mn distance $d \approx 0.26$ nm, below which the Mn moment is not stable. This value had been postulated for the first time for the Laves phases with manganese by Wada et al. (1987) and has recently been confirmed by Kim-Ngan et al. (1994) who gave a more precise value of 0.267 nm. However, as mentioned above, the magnetic properties of the ThCr₂Si₂ phases as well as the UMn_xAl_{12-x} alloys suggest that the band structure and geometry of the close environment of the Mn atom also have substantial influence. Moreover, the partial structural disorder in UMn₄Al₈ resulting from the permutation of the Mn and Al atoms between 8(f) and 8(j) sites reported by Bourée-Vigneron et al. (1990) could be the cause of the disappearance of the ordered magnetic moment. Although the Mn-Mn distance is just below the critical value (d = 0.255 nm), likely as in YMn₄Al₈ (d=0.256 nm) (Coldea et al. 1994b), the geometrical condition can prevent formation of a magnetic order. These authors claim that an increase in Mn concentration results in appearance of localized moment in the Mn sublattice. Their additional statement that the degree of localization changes with temperature is based on rather speculative arguments. On the contrary, an increase in x in the uranium alloys does not cause any remarkable change of character of magnetic behavior, although for UMn₃Al₉ there is an indication of magnetic ordering below 50 K (Suski et al. 1995). The 57 Fe Mössbauer probe studies of rare-earth compounds indicate that at 4.1 K the Mn sublattice is magnetically ordered. The low magnetic moment at 4.1 K and in 1.7 T (see table 7) and the shape of the magnetization curves show that both the R and the Mn subsystem transform to antiferromagnetic state.

The Mössbauer experiments carried out by Felner and Nowik (1979) on the lanthanide nuclei (¹⁵⁵Gd, ¹⁶⁶Er, ¹⁶¹Dy and ¹⁷⁰Yb) show that the hyperfine field is directed at an angle to the *c*-axis, and this observation suggests that the AF structure is not simple, collinear. Inelastic neutron diffraction experiments performed by Moze et al. (1990a) revealed a substantial influence of CEF on the properties of the Tb and Ho compounds. Elastic neutron examination of several lanthanide compounds shows that the 8(f) site is the majority site (93%) for the Mn atoms but 7% is occupied by Al atoms. The remaining 7% of the Mn atoms is not distributed statistically over the 8(j) and 8(i) sites but 5% of them enter into 8(j) sites while only 2% enter into 8(i) sites (Moze et al. 1990b). The unit cell volume of the RMn₄Al₈ compounds suggests that the compounds of Ce, Eu and Yb could be in a mixed-valence state (Felner and Nowik 1979). For the first compound this conclusion is confirmed by X-ray spectroscopy, where v=3.18, see table 3 (Shcherba et al. 1992). The experimental observation of ¹⁵¹Eu ME and the susceptibility curve above T_N indicate a mixed-valence state in EuMn₄Al₈ (Felner and Nowik 1979). In YbMn₄Al₈ Yb is predominantly divalent (Felner and Nowik 1979). The susceptibility of ThMn₄Al₈ follows a modified Curie–Weiss law resulting from pronounced contribution of the Pauli paramagnetism of the Mn sublattice. The susceptibility of UMn₄Al₈ does not follow a Curie-Weiss law and this behavior most probably is due to the competition of the itinerant conduction electrons of the U and Mn sublattices, and partly localized and partly hybridized 5f and 3d electrons, respectively. Elastic neutron diffraction excluded magnetic order in the uranium compound above 1.5K (Bourée-Vigneron et al. 1990) as mentioned above.

3.2.1.1.3. M = Fe compounds. The compounds of the (R, An)Fe₄Al₈-type have been investigated most frequently of all (R, An)M₄Al₈-type compounds. The results are collected in tables 8 and 9. One should note that this is the group of compounds in which several examples of single crystals are available (GdFe₄Al₈, Fujiwara et al. 1987; YFe₄Al₈, Chełkowski et al. 1991, Drzazga et al. 1994; DyFe₄Al₈ and HoFe₄Al₈, Drzazga et al. 1994; UFe₄Al₈, Stepień-Damm et al. 1984, Gonçalves et al. 1992). Some of the (R, An)Fe₄Al₈ compounds offer the unique possibility to perform ME examination on both the ⁵⁷Fe and the R or Np nuclei. These compounds can be divided into two distinct groups: In the first group, where R = La, Ce, Y, Lu and An = Th, only the Fe atoms carry a magnetic moment. According to a preliminary examination of these compounds the more or less sharp maxima in the temperature dependence of the magnetic susceptibility are interpreted as being due to AF ordering with the Fe moment oriented along the caxis (La, Ce, Buschow and van der Kraan 1978). In the second group (R = Eu, Gd, Yb), however, an angle is observed between the hyperfine field direction and c-axis (Felner and Nowik 1978). The conclusion about simple AF order for the first group is not valid here because the magnetic susceptibility of these alloys below $T_{\rm N}$ is markedly field dependent (Buschow and van der Kraan 1978), and even a tiny remanence at 4.2 K was observed for the Th compound (Suski 1989). In the paramagnetic region the susceptibility curves obey a modified Curie-Weiss law.

The compounds of the second group have two independent magnetic sublattices: one has Fe atoms ordered AF with magnetic moment oriented, according to ⁵⁷Fe ME (Buschow and van der Kraan 1978), along the c-axis at 4.2 K (Nd, Gd and Tb), and the second has R or An atoms where the R atoms order at a T_N which does not exceed 20K (Felner and Nowik 1978). The low magnetic moments at 4.2K and 1.7T (see table 8) in all the RFe_4Al_8 compounds indicate that both the Fe and R sublattices are initially AF coupled. In the majority of these compounds the temperature dependence of magnetization gives rise to a maximum at low temperature, with magnitude and location strongly dependent on the applied field strength. However, these maxima are absent if the samples are cooled down in the presence of a magnetic field prior to the magnetization measurements. In the high-temperature regime the susceptibility can be described by a Curie–Weiss law with the Θ and p_{eff} values collected in table 8. Single-crystal studies of the Dy, Ho and Y compounds (Drzazga et al. 1994) have revealed that at RT all investigated samples exhibit a small but nonnegligible torque of the sin 2θ -type, which is strongly influenced by the external field. It follows that a slight preference of easy magnetization direction (observed below $T_{\rm C}$) occurs in the temperature range treated as paramagnetic (above $T_{\rm C}$). This phenomenon may be associated with partial disorder of Fe and Al atoms. For R = Gd, Tb, Dy, Ho and Er there is another region below T_0 where the $\chi^{-1}(T)$ plot is linear (but T_0 is higher than the temperature of magnetic order), although the Θ and $p_{\rm eff}$ values are different from those found above T_0 . The effective moments

	aluminides
Table 8	RFe4Al8-type
	Ternary

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		с с	magn. state ^a	T _R (K)	$T_{ m Fe}$ (K)	$p_{\rm s}^{(\mu_{\rm n})}$	H_{hf} (T)	Ø	$p_{\rm eff}({ m R})$	$p_{\rm eff}({\rm Fe})$ ($\mu_{\rm a}$)	Remarks	Ref.
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0 5045					i						-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.5060		AF_{cc}^{a}		94	0.28 ^b		-16		4.6		- 71
SG ${}^{7}\text{Fe}$ Me, S; T_{so} follows $H^{2,2}$ (?) 4 AF 170 11.3 ${}^{7}\text{Fe}$ ME, Fe mainly in (§) 5 AF,WF 195 ${}^{1}\text{He}$ ME, Fe mainly in (§) 5 AF,WF 195 ${}^{1}\text{He}$ ME, Fe mainly in (§) 5 AF,WF 195 ${}^{1}\text{He}$ ME, Fe mainly in (§) 5 CAF 103 0.36 ${}^{1}\text{He}$ ME, ${}^{1}\text{CW}$, ${}^{1}\text{CT}$, ${}^{1}\text{CT}$, ${}^{1}\text{CT}$, ${}^{1}\text{CT}$ 6,7 CAF 103 0.36 ${}^{-68}$ 4.4 ${}^{9}\text{Fe}$ ME, ${}^{1}\text{CW}$, ${}^{1}\text{CT}$, ${}^{1}\text{CT}$, ${}^{1}\text{CT}$ 6,7 CAF 103 0.36 ${}^{-68}$ 4.4 ${}^{9}\text{Fe}$ ME, ${}^{1}\text{CW}$, ${}^{1}\text{CT}$, ${}^{1}\text{CT}$ 6,7 CAF 115 0.26 21 ${}^{9}\text{Fe}$ ME, ${}^{9}\text{CW}$, ${}^{1}\text{CT}$, ${}^{1}\text{CT}$ 2 CAF 115 0.26 23 ${}^{9}\text{Te}$ ME, ${}^{1}\text{CW}$, ${}^{1}\text{CT}$, ${}^{1}\text{CT}$ 2 AF 12 11.8(2) 11.8(2) 11.8(2) 2 AF 19 13.5 3.58 4.			l		184.7(2)		11.6(2)				⁵⁷ Fe ME, MCW	3
AF 170 11.3 7 Pe ME, Fe mainly in (8) 5 AF.WF 195 -145 -145 -145 6.7 6.7 AF.WF 195 -145 -145 6.7 $7 < 100$ K. WCW $T > 250$ K, $T < 0.7$ 6.7 CAF 103 0.36 -142 $7e$ ME, MCW $T > 250$ K, $T < 250$ K, $T < 10^{3}$ emu/mol 1 CAF 103 0.36 -68 4.4 $7r$ ME, MCW, $Prellic at 4.2$ K 2 CAF 115 0.26 23 4.2 $7r$ ME, MCW, $Prellic at 4.2$ K 2 CAF 115 0.26 23 4.2 $7r$ ME, MCW, $Prellic at 4.2$ K 2 AF 12 107 11.8(2) 3.58 4.2 $7r$ MCW, $Prellic at 4.2$ K 2 AF 19 137 0.18 $7r$ MCW, $Prellic at 4.2$ K 1 1 AF 19 107 0.18 $7r$ MCW, $Prellic at 4.2$ K 2 AF 19 107 11.3(2) 2			SG								⁵⁷ Fe Me, S; $T_{\rm SG}$ follows $H^{2/3}$ (?)	4
AF.WF 195 -145 49 sc. $\rho(T)$, $\chi^{-1}(T)$, WF at 6, $T < 100$ K, MCW $T > 250$ K, $T < 10^{-3}$ emu/mol 6/1 CAF 103 0.36 -68 4.4 $?r < 100$ K, MCW $T > 250$ K, $T < 10^{-3}$ emu/mol 1 CAF 103 0.36 -68 4.4 $?r < 100$ K, MCW $T > 250$ K, $T < 10^{-3}$ emu/mol 2 CAF 103 0.36 -68 4.4 $?r < ME$, MCW $P_{Pe} \ c$ at 4.2 K 3 CAF 115 0.26 23 4.2 $?r < ME$, MCW $P_{Pe} \ c$ at 4.2 K 3 CAF 115 0.26 23 4.2 $v = 3.28(5)$ 2 2 CAF 115 0.26 23 3 $v = 3.28(5)$ 3 3 CAF 10 118(2) 11.8(2) 11.8(2) 11.8(2) 2 2 AF 12 107 106 3 3 3 3 3 AF 19 137 0.18 3.3 3 3 3 2			AF		170		11.3				⁵⁷ Fe ME, Fe mainly in (8j)	5
$ \begin{array}{cccccc} {\rm CAF} & 103 & 0.36 & -68 & 4.4 & {}^{57}{\rm FeME}, {\rm MCW}, {\scriptstyle p_{\rm Fe}} \ {\it c} {\rm at} 4.2 {\rm K} & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & $			AF,WF		195			-145		4.9	s.e. $\rho(T)$, $\chi(T)$, $\chi^{-1}(T)$, WF at T < 100 K, MCW $T > 250$ K, $\chi_0 = -5.57 \times 10^{-3}$ emu/mol	6,7
$ \begin{array}{ccccc} {\rm CAF} & 103 & 0.36 & -68 & 4.4 & {}^{7}{\rm Fe}{\rm ME}, {\rm MCW}, p_{\rm Fe}\ ceq:eq:eq:eq:eq:eq:eq:eq:eq:eq:eq:eq:eq:e$	0.5075											1
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.5075		CAF		103	0.36		-68		4.4	⁵⁷ Fe ME	7
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$					135.4(2)		11.4(2)				⁵⁷ Fe ME, MCW, $p_{\text{Fe}} \parallel c$ at 4.2 K	3
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	0.5048											-
$ \begin{array}{c ccccc} \mbox{v} = 3.28(5) & \mbox{v} = 3.28($	0.5047		CAF		115	0.26		23		4.2		7
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$											valence state by X-ray spectroscopy, $v = 3.28(5)$	80
I59.7(2) I1.8(2) 5 Fe ME, MCW, $p_{\text{Fe}} \ c$ at 4.2 K 3 AF 12 107 1.06 35 3.58 4.2 1 AF 19 137 0.18 44 3.62 4.4 2 2 AF 19 137 0.18 44 3.62 4.4 2 2 AF 19 137 0.18 11.3(2) 3.62 4.4 3.62 4.4 2 AF 44 106 0.46 68 0.86 4.0 MCW 2											L _m -edge spectroscopy; $\rho(T)$, $\alpha(T)$	6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					159.7(2)		11.8(2)				⁵⁷ Fe ME, MCW, $p_{\text{Fe}} \ c$ at 4.2 K	ŝ
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.5058											1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.5054		\mathbf{AF}	12	107	1.06		35	3.58	4.2		7
AF 19 137 0.18 44 3.62 4.4 2 2 142(2) 11.3(2) 57 Fe ME, $p_{\rm Fe} \ c$ at 4.2 K 3 3 AF 44 108 0.46 68 0.86 4.0 MCW 2	0.5058											1
142(2) 11.3(2) 57 Fe ME, $P_{Fe} c at 4.2 K$ 3 AF 44 108 0.46 68 0.86 4.0 MCW 2	0.5054		AF	19	137	0.18		4	3.62	4.4		7
AF 44 108 0.46 68 0.86 4.0 MCW 2					142(2)		11.3(2)				⁵⁷ Fe ME, $p_{\text{Fe}} \parallel c$ at 4.2 K	Э
AF 44 108 0.46 68 0.86 4.0 MCW 2	0.5051											1
	0.5053		AF	44	108	0.46		68	0.86	4.0	MCW	7

W. SUSKI

	Ref.	2	5	10	11	ŝ	1	7	12	13	3	1	7	14	e	15	-	t page
	Remarks	Mixed valency on Eu, atomic positions	¹⁵¹ Eu ME, angle between <i>H</i> _{eff} and <i>c</i> -axis at 4.1 K is 62(5)°	XPS-3d core level, mixed valent	X-ray absorption near-edge, $v = 2.80(5)$ at 300 K	MCW		¹⁵⁵ Gd ME, angle between $H_{\rm hf}$ and <i>c</i> -axis at 4.1 K is 44(2)°	s.c. an easy axis at 4.2 K, spin reorientation temperature $T_{sR} = 20 \text{ K}$	⁵⁷ Fe ME, GdFe _{4+x} Al _{8-x} , Fe in 8f	⁵⁷ Fe ME, MCW, $p_{\text{Fe}} \parallel c$ at 4.2 K			$T_{R, \max} = f(H)$; T_{\max} may not be related to Tb sublattice	⁵⁷ Fe ME, MCW, $p_{\rm Fe} \parallel c$ at 4.2 K	ND: F(Tb),AF(Fe); no significant field effect on the (110) and (220), (211) intensities		continued on nex
	$p_{\rm eff}({\rm Fe})$ $(\mu_{\rm B})$	4.5						4.5					4.4					
	$p_{\rm eff}({ m R})$ $(\mu_{ m B})$	3.52						7.92			6.2		9.72		7.6			
1	ø S	-148						-151					-105					
e 8, continuec	H_{hf} (T)		14.8(4)					18.8(5)			10.1(2)				10.6(2)			
Table	$P_{ m s}$ $(\mu_{ m B})$	0.27						2.40					2.10					
	T _{Fe} (K)	137						130	170		172.3(2)		126		165.3(2)			
	T _R (K)							11	28				20			20		
	magn. state ^a	CAF						F,AF	ц				AF	SG		F,AF		
	c (nm)	0.5051					0.5048	0.5052				0.5043	0.5036				0.5037	
	a (mn)	0.8784					0.8758	0.8743				0.8749	0.8740				0.8715	
	~	Eu					Gd					Tb					Dy	

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES
c magn. $T_{\rm e}$ $T_{\rm ex}$ p	magn. T. T. D		$T_{r_{\rm e}}$		Tab	le 8, continue H _{xc}	p; Θ	<i>p.</i> .(R)	<i>p</i> (Fe)	Remarks	~
, (uu)	(mn)	state ^a	(K)	K K	$\mu_{\rm s}$ $(\mu_{\rm B})$	E)	(K) @	$P_{\rm eff}(\mathbf{x})$ $(\mu_{\rm B})$	$p_{\rm eff}(re)$	reinatks	
4) 0.8728	0.5050	AF	25	122	2.30		-80	10.6	4.2		
								8.1		MCW	
						−845(30) ^c				¹⁶¹ Dy ME	
0.8767(1)	0.5047(3)	cx	25(5)		3.6 ^d					ND, atomic positions, conical spiral structure of Fe sublattice, rotation ang of Fe moments ~45°	sle
										s.c., SG state in Dy and Fe sublattices	
				185						s.c., cusp in χ_{ac} below 100 K and maximum at 30 K	
0.8720	0.5035										
0.8720	0.5038		22	137	1.65		66	10.6	4.4		
								9.0		MCW	
0.8749(5)	0.5049(3)	сх	25		3.6 ^d					ND, atomic positions, conical spin structure of Fe sublattice, rotation ang of Fe moments $\sim 35^{\circ}$	le
0.8746(4)	0.5048(4)	F,AF								ND, F in Ho sublattice, $H \leq 6T$ at 4.2 K; $T_{SG} \approx 180$ K at Ho site; $P_s = 2$ /Ho atom at 16 K, $H = 0$, and 7.5/Fe atom at 4.2 K	
										³⁷ Fe ME, ND, transition to random SC state, $T_{od} = 40 \text{ K}$ (2 T) to 70 K (6 T); $P_s \approx 8$ at 6.0 T	(')
										continued on ne	8

W. SUSKI

	Ref.		15			5 7	1	5	20	÷	18	1	7	÷	-	7	20	3	×	6	:t page
) Remarks		ND under magnetic field; no F order at f site. $H = 2 T$ enforces F alignment of	randomly oriented Ho moments and transition from partly spiral to collinear	AF order for Fe moments	s.c., SG state in the Ho and Fe sublattice			¹⁶⁶ Er ME	⁵⁷ Fe ME, MCW	⁵⁷ Fe ME, Fe located mainly at 8f site and partly at 8i and 8i	•		⁵⁷ Fe ME, MCW			¹⁷⁰ Yb ME, angle between $H_{\rm hf}$ and <i>c</i> -axis is 40(5)°	⁵⁷ Fe ME, MCW	X-ray absorption, Yb valence $v = 3.00(5)$	L_{III} edge, χ_{g}^{-1} , $ ho(T)$, $lpha(T)$	continued on nex
	$p_{\rm eff}({\rm Fe})$							4.3					4.3			4.6					
	$p_{\rm eff}({ m R})$	Ĥ.						9.56		8.8			7.6			4.54					
~	@ \2							-38					7			62					
e 8, continuea	$H_{ m hf}$								1610(50)°	11.2(2)				11.1(2)			55.0(3)				
Tabl	$P_{\rm s}$	(84)						2.80					2.0 ^b			2.80 ^b					
	$T_{ m Fe}$	(w)						111		183.0(2)			109	186.6(2)		103					
	T _R (K)	3						25					20			80					
	magn. state ^a	אומום												\mathbf{AF}			AF				
	(mm)	(mm)					0.5037	0.5028				0.5034	0.5037		0.5026	0.5017(7)					
:	a (mn)	(IIIII)	<i>(p)</i>				0.8704	0.8700				0.8697	0.8688		0.8714	0.8691					
	R		Ho (<i>ct</i>				Er					Tm			γЪ						

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES

						Table	8, continue	<i>q</i>	ĺ		
, (m	a)	(um)	magn. state ^a	T _R (K)	$T_{ m Fe}$ (K)	$p_{ m s}$ $(\mu_{ m B})$	H _h (T)	(K) Ø	$p_{\rm eff}({ m R})$ $(\mu_{ m B})$	$p_{\rm eff}({ m Fe})$ Remarks $(\mu_{ m b})$	Ref.
0.86	89 0 87 0	.5036 .5030	AF_{cx}		97 197.3(2)	0.6 ^b	10.8(2)	62		4.3 ⁵⁷ Fe ME, MCW	3 5 -
c, complex. At 1.6 T and	d 4.1 K.						° In ^d Per	M c/s. - Fe ator	E		
<i>ferences</i> Buschow et Felner and A Buschow and A Felner and A Felner and A Chełkowski Drzazga et a	al. (1976) Nowik (19 d van der Vowik (19 Vowik (19 et al. (1994) il. (1994)) 778) Kraan (197 86a) 86b) 91)	(8)		 (8) Shcherba (9) Koterlin e (10) Malik er (11) Darshan (12) Fujiwara (13) Kamimo (14) Felner ar 	et al. (1992) tt al. (1993) al. (1981) and Padalia (et al. (1987) ri et al. (1988) rd Nowik (196	1984) ;) 88)			 (15) Schäfer et al. (1991) (16) Schäfer and Will (1983) (17) Talik et al. (1993) (18) Schäfer et al. (1989) (19) Gal et al. (1989) (20) Felner and Nowik (1979) 	

are slightly below the corresponding free-R-ion values. At temperatures below T_0 the susceptibility shows no or only a weak field dependence. For R = Pr, Nd, Sm, Tm and Yb, the $\chi^{-1}(T)$ plot also changes its slope below T_0 , however, this plot is nonlinear and exhibits an apparent sensitivity to the annealing of samples. In all RFe₄Al₈ systems the effective moments of the Fe atoms in the paramagnetic region are larger than the value resulting from the saturation moment of Fe. Buschow and van der Kraan (1978) took this as an indication that the 3d electrons in these compounds have a fairly large degree of itineracy. The same authors reported that for all RFe₄Al₈ the temperature dependence of the magnetic susceptibility can be described by a modified Curie–Weiss law (MCW).

Experimental observation of the ¹⁵¹Eu Mössbauer spectra in EuFe₄Al₈ and the unit cell size indicate that the Eu ion is in the mixed-valence (MV) state. However, at low temperature it behaves like an Eu³⁺ ion due to the hyperfine field of the Fe sublattice acting below ordering temperature (Felner and Nowik 1978). Also, XPS-3d core level spectroscopy (Malik et al. 1981) and X-ray absorption near edge structure (XANES) results (Darshan and Padalia 1984) showed the Eu ion to be in the MV state with v=2.80 at 300 K. In turn, both unit cell size volume (Felner and Nowik 1978) and X-ray spectroscopy show that the Ce ion is in the MV state as well, and the valence v amounts to 3.28 (Shcherba et al. 1992).

More advanced methods have been used in investigations of the (R, An)Fe₄Al₈-type compounds, particularly in single-crystal form (see e.g. Fujiwara et al. 1987, Chełkowski et al. 1991, Drzazga et al. 1994). These methods show some new details of the magnetic properties of these materials; for example, a spin reorientation has been discovered in GdFe₄Al₈ single crystals. As one can see from fig. 11, at 4.2 K the *a*-axis is the easy axis. Above the spin-reorientation temperature $T_{SR} = 20$ K the easy axis tilts away from the *a*-axis, up to the Curie point $T_C = 28$ K (Fujiwara et al. 1987). A similar conclusion has been drawn by Drzazga et al. (1994) from the investigation of YFe₄Al₈ single



Fig. 11. Magnetic (θ, T) phase diagram of GdFe₄Al₈. θ is the tilting angle of the easy axis with respect to the *a*axis in the *a*-*c* plane. Closed and open circles are experimental points obtained under applied fields (H_a) of 0.46 and 1.83 T, respectively. The dotted curve represents "spontaneous" tilting under $H_a = 0$ (Fujiwara et al. 1987).

crystals by torque magnetometry. They claim that the easy direction of magnetization changes from the (101) plane to the direction perpendicular to this plane at about 160 K under a magnetic field of 1.6 T. The temperature range of spin reorientation corresponds to a flat maximum of the $\chi(T)$ plot interpreted as the AF transition by Moze et al. (1990c).

For DyFe₄Al₈ and HoFe₄Al₈, neutron diffraction experiments exclude the possibility of a magnetic ordering in the lanthanide sublattice, and for both compounds only one magnetic phase transition, at about T = 25 K, is found, below which the iron moments form a conical spin structure with the propagation vector of the spiral along [110] and the rotation angle of the Fe moments about 45° and 35° for the Dy and Ho compounds, respectively. The magnitude of the ordered Fe moment is $3.6\mu_{\rm B}/{\rm Fe}$ atom at 4.2 K (Schäfer and Will 1983). It might be that the cause of the high-temperature anomaly observed in magnetic measurements is the formation of a spin-glass state (SG) which coexists with magnetic order at low temperature (Schäfer et al. 1989, Gal et al. 1989). A single-crystal examination of these compounds by Drzazga et al. (1994) confirms the formation of the SG state in both the R and the Fe sublattices, and at the same time indicates that the aaxis is the easy magnetization direction. For DyFe₄Al₈ single crystals a thermomagnetic effect was found below 30K (Talik et al. 1993). A strong anisotropy of the magnetic susceptibility occurs over the whole temperature range and is especially pronounced at low temperatures. A T^2 dependence of the electric resistivity in the temperature range 4.2– 100 K and an AF transition at 185 K were found. A cusp in the $\chi_{ac}(T)$ plot was observed below 100 K with a maximum at 30 K. Schäfer et al. (1989) claim that in HoFe₄Al₈ the SG state is also established below 180K. Moreover, a transition from aligned to random SG state is reported at $T_{OG} = 40-70$ K, depending on the applied magnetic field. However, the most unusual feature is the lack of cusp (or an extremely broad cusp) in the ac susceptibility in the vicinity of T_{SG} (Gal et al. 1989). The SG state in this compound as well as in compounds with R = Tb, Er and Dy exists as a result of competition of different types of magnetic interactions in these compounds. The same reasoning is applied to UFe₄Al₈ (Gal et al. 1990), although the deficiency in the Al sublattice (AnFe₄Al_{8-x}) is also considered as the cause of the SG state both in UFe₄Al₈ and in ThFe₄Al₈ (Gal et al. 1990).

A high Néel point (~195K) was reported by Chełkowski et al. (1991) for single crystals of YFe_4Al_8 , together with weak ferromagnetism below 100 K. These two singular points were confirmed by anomalies in the temperature dependence of the electric resistivity (Chełkowski et al. 1991). Since neither neutron diffraction nor Mössbauer effect examination were performed on this material we are reluctant to draw a final conclusion here.

In actinide compounds (see table 9), ThFe₄Al₈ is considered as the nonmagnetic standard for the actinide sublattice because the Th sublattice is nonmagnetic. The magnetic transition temperature reported by Buschow and van der Kraan (1978) was also confirmed by neutron diffraction (temperature dependence of the [110]-peak intensity) (Ptasiewicz-Bak et al. 1988). However, other neutron diffraction examinations along with magnetic ac and dc susceptibility and Mössbauer effect investigations (Gal et al.

						Ternary	T ∕ AnFe₄,	able 9 Al _s -type alı	uminides		
An	a (nm)	c (nm)	magn. state	T _{c,N} (K)	$p_{\rm s}$ $(\mu_{\rm B})$	p_0 $(\mu_{\rm B})$	Ø	$P_{ m eff} \ (\mu_{ m B})$	H _{hf} (T)	Remarks	Ref.
fI	0.8842	0.5076	AF	(0)6 141					(1) 2(2)	XRD 57Ea MF MCW v ⁻¹ = -15.6 mol/vm ³	-
	0.8831	0.5095	đ	(7)7.141				3.5	(7)711		4 m
	0.8827(1)	0.5095(1)	AF			0.7(1)				ND, atomic positions	9 4
			SG	110(20)					11.4(5)	ND; ⁵⁷ Fe ME	S
			AF_{cx}			1.6(4)				ND	9
D	0.8749	0.5036								s.c., XRD	7
	0.8736(1)	0.5046(2)	AF			1.0(1) ^c				ND, atomic positions, G-type Fe sublattice	4
			ц			$0.8(1)^{a}$				U sublattice	
			ц				160	7.08		CW law above 200 K	œ
			Fi. G	160		1.6				UN	9
			SG	140		$0.86(6)^{4}$		10.8(5)		⁵⁷ Fe ME, ND: relative occupation of Fe atoms	S
										(mostly 8f)	
										ND under magnetic field up to 8 T, no influence	6
				150	1.8					s.c., ND, easy <i>a-b</i> plane, magnetization,	10
										polarized ND	
*dN	0.8759(6)	0.5055(8)								NpFe ₄ Al _{9-x} , (x = 1.6): ND, atomic positions	4
			SG	118(5)		$0.6(6)^{b}$			9.5(5)°	⁵⁷ Fe ME, ND relative occupation, SG in Fe	S
									159 ^b	sublattice and nonequivalent Np sites, ND under	
										magnetic field $H = 5 T$	
			AF F	130(10)		1.05(15)° 0.6 ^b			9.5(5)°	⁵⁷ Fe ME	П
			4	(01)011		0.0					
* Va	riable compo	sition; see R	Remarks	column.				b At N	чр.		
^a At	ü.							° At F	ف		
Refe	rences										
а (uschow et al.	(1976) m der Venan (1	1078)		(5) (5) (6) (6)	al et al. (1990 veianvior Bob)) af 21 /10	(00)		(9) Schäfer et al. (1991)	
9 B	aran et al. (19	85)	(0/61		(0) Ste	asicwicz-Dan	et al. (19	84)		(10) raivau et al. (1774) (11) Gal et al. (1987)	
(4) S	chäfer et al. (1	(686)			(8) Ba	tran et al. (19	83)				

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES

1990) have suggested a SG state below 110 K. The difference in reported transition temperature can result from the number and distribution of vacancies caused by different thermal histories.

Neutron diffraction shows that below ~145 K UFe₄Al₈ exhibits a complicated magnetic structure in which there is AF ordering in the Fe-8(f) sublattice and ferromagnetic ordering in the U-2(a) sublattice (Gal et al. 1990). The Fe sublattice exhibits a configuration with the spin orientation along the c-axis and moment values of $1.0\mu_{\rm B}/{\rm Fe}$ atom, whereas the ferromagnetic U sublattice contributes with a magnetic moment of $0.8\mu_B/U$ atom (Schäfer et al. 1989). Neutron diffraction studies show that magnetic reflections are not enhanced significantly under magnetic field below 7T (Schäfer et al. 1991). The ordered 5f moments are so small that a variation in magnitude or orientation cannot be seen on polycrystalline material (Schäfer et al. 1991). The conclusion about the small influence of magnetic field on the neutron diffraction pattern does not agree with the high-field magnetic measurements (Suski 1989). Neutron diffraction experiments performed on a single-crystal sample of UFe₄Al₈ (Paixão et al. 1994) did not confirm the SG state but showed AF +-+- type arrangements of the Fe moments propagating along the a and b axes with a ferromagnetic component on the U sublattice. Two polarized neutron scattering experiments performed under a field parallel to the caxis and along the b-axis showed an induced magnetic moment of $\sim 0.18 \mu_{\rm B}$ in the Fe atom and less that $0.04\mu_B$ in the U atom for the first experiment and $0.25\mu_B$ for both the U and Fe atoms in the second. Magnetization measurements on the same sample have shown an easy a-b-plane magnetization. A remanent magnetization of $1.8\mu_{\rm B}$ /fu is found at 4.2 K for a field parallel to the *a*-axis whereas no significant remanent magnetization is found for a field parallel to the c-axis. The above results suggest that the anisotropy type (easy direction) strongly depends on the f-electron metal. For UFe_4Al_8 and $NpFe_4Al_8$ the SG state has been reported by Gal et al. (1990) to coexist at low temperatures with ferromagnetic order in the actinide sublattice and AF order in the Fe sublattice. This coexistence of both types of magnetic ordering, as well as the vacancies in the Al sublattices, can be the origin of the SG state. The ordered magnetic moment for Np is $p_0 = 0.6(6) \mu_B/Np$ atom (Gal et al. 1990). The susceptibility of ThFe4Al8 follows a modified Curie-Weiss law (Buschow and van der Kraan 1978) with effective magnetic moment $p_{\text{eff}} = 3.5 \mu_{\text{B}}$ (Baran et al. 1985), while the temperature dependence of the magnetic susceptibility of UFe₄Al₈ obeys a Curie-Weiss law above $\sim 200 \, \text{K}$.

3.2.1.1.4. M = Cu compounds. The magnetic properties of the (R, An)Cu₄Al₈ systems are collected in table 10a. These compounds, except for those with Ce, Eu, Yb, Lu, Y, Th and Np, exhibit AF character (Felner and Nowik 1979). In CeCu₄Al₈ the Ce ion is trivalent and the compound exhibits paramagnetic behavior, and no sign of superconductivity or of magnetic ordering could be detected down to the lowest accessible temperature (Rauchschwalbe et al. 1985). However, the temperature dependence of the resistivity has a peak at 6K corresponding to a positive peak at 8K in the thermoelectric power and a single peak in C/T versus T near $T_{max} = 0.4$ K with γ amounting to 300 mJ/K² mol. This value suggests that this material could be a Kondo system (Rauchschwalbe et al. 1985).

	Ref.		5	ŝ	4	4	1	7	7	7	2	1	ŝ	7	9	ы	7	7	٢	5	page
SO	Remarks		⁵⁷ Fe ME	$\rho(T)$, no SC and magnetic order, $\alpha(T)$ peak at 8 K, Kondo system (?), <i>C/T</i> vs. <i>T</i> double peak, $\gamma = 300 \text{ mJ}/(\text{mol } \text{K}^2)$	XPS, $v = 3.00(5)$	$L_{\rm HI}$ absorption edge, $\chi(T)$, $\rho(T)$, $T_{\rm max} \approx 15$ K, increase of χ with T , with $T_{\rm max}$ at about 450 K, $\alpha(T)$			⁵⁷ Fe ME		¹⁵¹ Eu ME			¹⁵⁵ Gd ME, angle between $H_{\rm hf}$ and c -axis	ESR	⁵⁷ Fe ME	161 Dy ME			1 166 Er ME	continued on next
luminid	. ^н ()													l 6.6(4)			50(30) ^a			50(150) ²	
0a s-type a	ΗU																11			13.	
Table 1 L,An)Cu ₄ Al	$P_{ m eff}$ $(\mu_{ m B})$		2.62					3.56	3.58) 1.00				7.89		9.50	10.6	10.9		9.8	
Ternary (F	(K)		-17					-15	-18	-40(5			-16	-16		-14	. 2	L		-10	
	$P_0 \ (\mu_{ m B})$																				
	$T_{\rm N}$ (K)							15	20	~25			32	32		22	17	٢		9	
	magn. state							AF	AF	\mathbf{AF}			AF			AF	AF	AF		AF	
	с (nm)	0.5139	0.5153	0.518			0.5157	0.5150	0.5143	0.5143	0.5156	0.5146	0.5139	0.5146		0.5134	0.5135	0.5122	0.5119	0.5130	
	(nm)	0.8721	0.8839	0.885			0.8806	0.8817	0.8789	0.8797	0.8886	0.8748	0.8756	0.8746		0.8752	0.8725	0.8720	0.8691	0.8712	
	R/An	ک جر ا	3				Pr		ΡN	Sm	Eu	Gd				Τb	Dy	Но	Er		

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES

a c maan T s	r maan 7 r	maan T.	т С	0	0		Table 10a, con	ntinued	-	'
	a (mi)	с. (шш)	state	¹ N(K)	p_0 $(\mu_{ m B})$	K a	$p_{ m eff} \ (\mu_{ m B})$	$H_{\rm hf}$	Remarks	
00	0.8674	0.5114	AF	S		-9	7.76			1
	0.8819	0.5084								
0	0.8746	0.5122	WTDP						¹⁷⁰ Yb ME	
									XPS , $v = 2.47(5)$	
									L _{III} –absorption edge, $\chi(T)$, increase above 200 K, maximum at 430 K, minimum at about 200 K; $\alpha(T)$	~
0	0.8670	0.5098	WTDP							
									CeAg ₄ Al ₈ : no magn. and SC	
0	0.8818	0.5165								
									$\operatorname{ThCu}_{4.5}\operatorname{Al}_{7.5}$; $\rho(T)$	
_ د	9/.8.(0.510								
									$\rho(T)$, no SC and magnetism	
0	.8792	0.5122	AF	30		-138	3.11		$UCu_{4,5}Al_{7,5}\colon^{63}Cu$ NMR, lack of resonance, CW at $40\to180\mathrm{K}$	
									CEF scheme, $\Delta = 85$ K, W = 30 K, doublet-singlet, HF ?	
			AF	37(2)	1.3(5)				ND	
			HF?						$\rho(T)$, $C(T)$, $\gamma = 118$ mJ/mol K ² , diffuse maximum a 25 K	÷+
									point contact spectroscopy, no indication of HF stat	d)
									continued on n	8

180

W. SUSKI

					E	able 10a, <i>co</i>	ntinued		
R/An a (nm)	<i>с</i> (пп)	magn. state	$T_{\rm N}$ (K)	P_0 $(\mu_{ m B})$	Ø	$P_{ m eff}$ $(\mu_{ m B})$	$H_{\rm hf}$ (1)	Remarks	Ref.
(x) f	<i>f</i> (x)	AF			č			ND, atomic positions UFe,Cu _{t-x} Al ₈	14 15
					-2/8 -149	3.59 ^b		c.u = x 0.1 = x	ci 15
					399 252	7.29 ^ի 5.72 ^ի		x = 2.0 x = 3.0	15 15
Np 0.8800(6	0.5065(8)	Pc					300	ND, atomic positions ²³⁷ Np ME, magn. hyperfine splitting below 45 K related to slow paramagnetic relaxation	16 17
* Variable com ^a In Mc/s.	osition; see 1	Remarks o	column.				^b Per fu. ^c Down to 2	K	
References (1) Buschow et al (2) Felner and No (3) Rauchschwalb (4) Shcherba et al (5) Felner and No (6) Coldea et al. (. (1976) wik (1979) e et al. (1985) . (1992) wik (1978) 1994a)			(7) Ko (9) Dn (9) Co (10) Bu (11) Bu (12) Ph	terlin et al. (Jis et al. (19 rdier et al. (1) aran et al. (1 aran (1988) araiewicz-Bął	1993) 89) 985) 986) ¢ et al. (1988)		 (13) Naydyuk et al. (1993) (14) Krimmel et al. (1992) (15) Suski et al. (1992a) (16) Gal et al. (1987) (17) Gal et al. (1985) 	

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES



Fig. 12. Néel points, T_N , of RCu₄Al₈ compounds, versus lanthanide element, R. The solid line is proportional to the de Gennes factor $(g_J - 1)^2 J(J + 1)$ (Felner and Nowik 1979).

The magnetic susceptibility of YbCu₄Al₈ and LuCu₄Al₈ is low and almost independent of temperature (Felner and Nowik 1979), however, some anomalies have been detected in the $\chi(T)$ plot by Koterlin et al. (1993) for the former compound, for which XPS experiment revealed mixed valence with v=2.47 (Shcherba et al. 1992). In turn, as mentioned above, Ce in CeCu₄Al₈ is trivalent (Felner and Nowik 1979, Shcherba et al. 1992) and Eu in EuCu₄Al₈ is divalent (Felner and Nowik 1979). As mentioned at the beginning of this section the AF structure is not necessarily simple, because for GdCu₄Al₈ a 155 Gd ME experiment revealed an angle between the direction of hyperfine field and c-axis $(\delta = 60(0)^{\circ}$, Felner and Nowik 1979). The magnetic susceptibilities of the antiferromagnets are described above T_N by modified Curie–Weiss laws, and the Weiss constants Θ , turn out to be negative, which is consistent with the AF order. Since the magnetic order in RCu₄Al₈ compounds is due to the f-electron element interactions it seems reasonable to look for a correlation between T_N and the de Gennes factor $(g_J - 1)^2 J(J + 1)$. As one can see from fig. 12 (Felner and Nowik 1979) this correlation holds reasonably well for the heavier lanthanides, whereas for lighter ones there is a pronounced discrepancy. This discrepancy results probably from CEF effects and from the stronger contribution of the conduction electrons and magnetocrystalline anisotropy than accounted for in a simple RKKY approach.

As concerns the actinide compounds, ThCu₄Al₈ is nonmagnetic while UCu₄Al₈ is antiferromagnetic below ~40 K and with ordered magnetic moment ~1.3 μ_B (Ptasiewicz-Bak et al. 1988). This Néel point is the highest in the whole series of (R, An)Cu₄Al₈ compounds and this phenomenon is normal because the exchange interactions in the uranium compounds are much stronger than in the corresponding lanthanide compounds. The value of the ordered magnetic moment is also high in relation to other uranium intermetallics and could result from weak CEF or hybridization interactions.

The system $UCu_{4+x}Al_{8-x}$ is generally puzzling and will be discussed below.

NpCu₄Al₈ is paramagnetic down to 2K as has been shown in ME (Gal et al. 1985) and ND (Gal et al. 1987) examinations.

As mentioned above, $CeCu_4Al_8$ exhibits strongly enhanced γ (Rauchschwalbe et al. 1985), although this value is still higher in the $UCu_{4+x}Al_{8-x}$ alloys. Also other systems



Fig. 13. UCu_{4+x}Al_{8-x} alloys: relations between concentration x and (upper panel) coefficient of the electronic specific heat, γ ; (middle panel) ratio between electric resistivities at $T_{\rho_{\text{max}}}$ and at RT, $\rho_{\text{max}}/\rho_{300 \text{ K}}$; (lower panel) Néel points, T_{N} , or temperature of maximum in $\rho(T)$ plot, $T_{\rho_{\text{max}}}$. (Geibel et al. 1990.)

seem to exist in broad composition range but the Fe alloys will be discussed in a separate subsection because their properties were examined for few systems containing Y or felectron elements. We have at present also some indication that the $UMn_{4+x}Al_{8-x}$ system exhibits a range of homogeneity for $-1.0 \le x < 3$ in which paramagnetic properties are observed for x > -1 (Suski et al. 1995). For UCu_{4+x}Al_{8-x} a neutron diffraction experiment (Ptasjewicz-Bak et al. 1988, Krimmel et al. 1992) revealed simple AF ordering in the U sublattice for x not far from 0, but the temperature dependence of specific heat did not demonstrate the λ -type anomaly typical for magnetic ordering (Drulis et al. 1989). The electronic specific heat coefficient γ obtained in this experiment amounts to about $120 \text{ mJ/K}^2 \text{ mol}$ for $x \approx 0.5$. However, for $x \approx 1.5$ the magnetism disappears and γ increases to 800 mJ/K² mol, suggesting heavy-fermion like behavior (Geibel et al. 1990). The Néel points and γ values versus concentration x, are shown in fig. 13. The reason for such a high γ value is a mystery since the material does not transform to the superconducting state at low temperature (Rauchschwalbe et al. 1985). Pointcontact spectroscopy does not provide any indication of HF-state (Naydyuk et al. 1993). Structural disorder as the reason for both a high γ and the absence of magnetic ordering

	Magnetic data for U	$JFe_{x}Cu_{4-x}Al_{8}^{a}$	
x	<i>Ө</i> (К)	$p_{ m eff} \ (\mu_{ m B}/{ m fu})$	
0.5	-278	3.63	
1.0	-149	3.59	
2.0	-399	7.29	
3.0	-352	5.72	

1.04

^a Data from Suski et al. (1992a); see also table 10a.



Fig. 14. Magnetic susceptibility of UFe_xCu_{4-x}Al₈ alloys: χ_M versus temperature T < 100 K measured in a magnetic field of 0.7T (Suski et al. 1992a).

and superconductivity has been excluded by a recent neutron diffraction experiment (Krimmel et al. 1992). It might be that the increase of Cu concentration causes a volume compression, which is not large enough to decrease the U-U separation below the Hill limit necessary for superconducting state, but which might result in an enhanced 5f-ligand hybridization, and in the spirit of the Doniach (1977) phase diagram the 5f conductionelectron exchange coupling constant is shifted from below to above the critical value at which AF order vanishes. At this point we should mention that $UNi_{10}Si_2$, which will be discussed in detail later, also exhibits an enhanced $\gamma \approx 100 \text{ mJ/K}^2 \text{ mol}$ (Suski et al. 1993d).

The UCu_{4+x}Al_{8-x} system has been obtained in the form of amorphous thin film. From ac resistivity measurements it follows that compared to the results in the crystalline bulk alloys, the onset of magnetic order is suppressed at low Cu concentrations, while the onset of a coherent heavy-fermion state is suppressed at high x. The system reveals a single-ion Kondo behavior down to the lowest temperatures, but significant deviations were detected from the behavior of dipolar Kondo system (Lunkenheimer et al. 1994).

Finally we discuss the UFe_xCu_{4-x}Al₈ system (Suski et al. 1992a). A ThMn₁₂-type phase has been observed for all values of x. At temperatures above 400 K the susceptibility follows a Curie–Weiss law. The respective magnetic data are listed in table 10b.

One can see that for low Fe concentration these parameters look reasonable, but for x > 1.0 they are strongly enhanced. Most probably, their magnitude reflects the presence of iron. The temperature dependence of the susceptibility below 100 K is presented in fig. 14. One can see that it is difficult to determine which type of magnetic ordering, if any, exists in this temperature range. The SG state reported for UFe₄Al₈ (Gal et al. 1990) can be enhanced in the UFe_xCu_{4-x}Al₈ solid solutions, and the difference in behavior between FC and ZFC samples (see fig. 4 in Suski et al. 1992a) seems to indicate such a possibility. Also, magnetic ordering of both UCu₄Al₈ and UFe₄Al₈ complicates the establishment of the low-temperature properties of their solid solutions. This system seems to be extremely interesting, however, it needs still careful examination.

3.2.1.2. $(R, An)Fe_5Al_7$ -type compounds. As mentioned above, the 1:5:7 stoichiometry is observed in the rare-earth compounds with Fe. Moreover, it is obtained only for heavier lanthanides (from Sm to Lu), Y and U. Tables 11a,b list the results of crystallographic and magnetic investigations (table 11a) and of Mössbauer effect and neutron diffraction examination (table 11b). Both sets of experiments indicate that the excess iron atoms enter predominantly the 8(j) position (Felner et al. 1983, Kockelmann et al. 1994). Moreover, Schäfer et al. (1994) also report indications for clustering of the Fe atoms on 8(j) positions. Magnetic investigations indicated a single transition of the Fe and R sublattices for these compounds at a temperature between 200 and 250 K (Felner et al. 1983). A ferrimagnetic structure has been proposed on the basis of the observed minimum in the temperature dependence of the magnetization (a compensation point?) for Sm, Tb, Dy, Ho and Er compounds. This structure has been confirmed for the compounds of Tb, Dy, Ho, Er and Tm in the ND experiment by Kockelmann et al. (1994), but at the same time the Néel points for the Ho and Er compounds were found to be lower, 61(1) and 62(1) respectively, than that determined in magnetometric examination; also, in the case of $ErFe_5Al_7$, T_N is lower than the compensation point (see tables 11a,b).

According to magnetic measurements (Felner et al. 1983) the low-temperature behavior of some of these compounds is very strange. $SmFe_5Al_7$ exhibits large magnetic and

R I	c (mm)	magn.	T ^{mag} a ord	T ^{ME a} ord	T _{comp} b (W)	H _e	Ti Ty RFe ₅ .	able 11a Al ₇ -type Θ	$p_{\rm eff}$	ides $p_0(\mathbf{R})$	easy	$p_0(\mathrm{Fe})$	Remarks ^d	Ref.
E 0	(III)	State	±10	±10 (K)	∓2 (¥	(1) 土0.03	$(\mu_{\rm B})$	£€	$(\mu_{\rm B})$	$(\mu_{\rm B})$	dir.	$(\mu_{\rm B})$		
0	5026	ė	215	165		2.0	5.8	230	4.4					
o.	5056	Εï	220		185°	13.6	5.1	265	3.9					. –
o.	5025	Fi	268	260		0.4	0.4 ^f	241	3.8				¹⁵⁵ Gd ME	. –
o.	5026	E	248	240	60	6.3	0.6	174	2.5					
0	5052	F	235							8.12(9)	$\frac{c}{1}$	1.64(6)	ND. atnos. Fe8f	~
0	5020	Ξ	227	225	93	24.3	1.8	177	3.4					-
			230(23)							9.5(1)	<i>с</i> Т	1.60(8)	ND. atnos. Fe8f	
0	5014	H	227	210	67	9.5	2.3	186	3.5	~				ı —
Ö	5043	Ë	61(1)							6.29(8)	0	1.65(4)	ND, atpos, Fe8f	. 6
			200							· ·	:	× /	ND, coexisting SRO/LRO	ŝ
			60											
0	5009	E	218	215	29	18.5	1.7	192	3.6					. –
o.	5029	ï	62							8.96(8)	Τc	1.78(5)	ND. atnos. Fe8f	. 6
0	5001 [£]						0.5	109						ı
0.	5046	Fi	235(20)							9.79(8)	† c	1.21(5)	ND. atnos. Fe8f	~
0	5008	ċ	207	180		2.0	3.6	224	3.9	2			the forth of the forther that the second sec	ı –
ö	4988	ċ	212	165		2.0	5.4	224	4.2					
npera	ature 1	from ma	ignetic (T_{on}^{m})	ag) and	from MH	$\Xi (T_{ord}^{ME})$		P	atpos, al	omic pos	itions: F	e8f. Fe m	tinlv in 8(f).	
			I					0 0	Only wh	ien coolec	l within	seconds in	n small field.	
л Iel 2 К.	mpera	iture.						- 60	In 1.8 T. Contains	a second	l unider	tified nha	ą	
(198	6				(2) Kocł	kelmann e	t al. (199-	4)			(3) Ha	levv et al. (1994)	
												•		

186

W. SUSKI

				Mö	ssbauer ai	nd neutron	Table 1 diffraction d	1b ata for RFe ₅ Al	,-type alum	inides			
2	$N_{\rm f}{}^{\rm a}$	Nia	Nia	H _{hf}	β ^b	¢.	magn.	T _c	$P_0^{\rm R}$	$P_0^{\rm Fe}$	easy	Remarks	Ref.
		'n		Έ		۵	state	(K)	$(\mu_{\rm B})$	$(\mu_{\rm B})$	dir.		
		土2%		±0.6		±5°							
۲	53	40	7										1
Sm	63	34	æ										1
Gd	53	44	ŝ									on ⁵⁷ Fe	1
				27.7 ^d		40						on ¹⁵⁵ Gd	1
Ъ Р	56	39	5										1
	83	15.1	1.4		0.53		Fi	235(10)	8.12(9)	1.64(6)	тc	Incompatibilities ^e	6
Dy	53	39	×										1
								230(23)	9.5(1)	1.60(8)	Τc		7
Ю	58	38	4										-
	80.7	16.8	2.5		0.34		H	61(1)	6.29(8)	1.65(4)	$\ c$	Incompatibilities ^e	7
								200 ^f					3
								60					ŝ
Er	52	41	7										1
	83.6	15.0	1.3		0.34		H	62(1)	8.96(8)	1.78(5)	тc	Incompatibilities ^e	7
Τm	84.1	14.7	1.2		0.83		H	235(20)	9.79(8)	1.21(5)	тc	Incompatibilities ^e	6
Υb	52	38	10										-
Lu	62	36	7										-
^a Popi ^b Criti	lation of F cal expone	e sites. nt. U and o						^d At 4.2 K. ^e Incompatible ^f Coevistence	e occupancy of long- ar	y values may	result fro	om stoichiometry devia	tion.
SIIV										0			
Refere (1) Feli	<i>inces</i> ner et al. (15	83)			(2) Kc	ockelmann e	st al. (1994)		(3)	Halevy et al. ((1994)		

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES

thermal hysteresis and time-dependent effects. The temperature dependence of $GdFe_5Al_7$ magnetization displays a broad maximum. A negative magnetization is also observed for compounds of Tb, Dy, Ho and Er at low temperatures when the sample is cooled down in a magnetic field. In addition, magnetization curves with compensation (?) points, sharp maxima, and strong hysteresis phenomena are detected. Time-dependent effects are also observed for the Dy and Er compounds (Felner et al. 1983). ⁵⁷Fe Mössbauer studies reveal at least three magnetically nonequivalent sites. Felner et al. (1983) propose the following magnetic structure for the investigated compounds: the Fe atoms at the 8(f) site, the majority iron site, form a canted AF structure with a ferromagnetic component antiparallel to the rare-earth sublattice magnetization. The Fe atom at the 8(j) site also has its moment antiparallel to the rare-earth moment. Iron at the 8(i) site stays nonmagnetic even at 4.2 K. In compounds with a nonmagnetic R the 8(j)-sublattice magnetization is antiparallel to the 8(f)-site ferromagnetic moment. Felner et al. (1983) claim that within this assumed spin structure the features of observed magnetization curves can be explained. One can accept this explanation for the zero-field state, but the processes observed under nonzero field need further elucidation and the time-dependent effects might be related to the spin glass state.

Neutron diffraction (Kockelmann et al. 1994) provides a slightly different picture of magnetic structure. At lower temperatures there is ferrimagnetic long-range order with the magnetic moments of the R sublattice antiparallel to the Fe moment at site 8(f). Ordered magnetic Fe moments at the 8(j) site oriented parallel to those on 8(f) sites can be considered seriously. Moreover, TbFe₅Al₇ exhibits weak satellite reflection below 100K in addition to the ferrimagnetic order; these satellites result from a modulation of the ferrimagnetic structure along a basal-plane direction with a modulation length of about 20 unit cells. All compounds exhibit broad peaks due to diffuse magnetic scattering at a position near the Bragg reflections. These diffuse peaks can be attributed to short-range ferrimagnetic ordering which occurs well above the Curie points. The short-range order may result from a clustering of the Fe atoms in 8(j) positions. The critical exponents β presented in table 11b exhibit a large scatter and cannot be attributed to any universal mechanism of exchange interactions (Kockelmann et al. 1994). Coexistence of short- (SRO) and long-range magnetic order (LRO) below 200 K was also proposed by Halevy et al. (1994) to exist in HoFe₅Al₇; this is transformed in only LRO at about 60 K.

As concerns UFe₅Al₇, magnetic measurements by Baran et al. (1985) (table 11c) suggest it to be ferromagnetic below 268 K. This conclusion has been confirmed by recent ⁵⁷Fe ME experiments (Vagizov et al. 1995). However, the low value of saturation magnetic moment calculated per Fe atom, $p_s = 1.23\mu_B$, hints at a possibly complex ferromagnetic structure (table 11b). ⁵⁷Fe ME examination revealed that Fe atoms occupy mostly 8(f) (54%) and 8(j) sites, whereas the 8(i) position is populated only by a small fraction (3%) (Vagizov et al. 1995). The total magnetic moment determined in this experiment amounts to $0.814\mu_B$. The difference between the latter value and the saturation magnetic moment obtained from magnetic measurements (Baran et al. 1985) suggests the possibility that the uranium sublattice contributes to the magnetic ordering.

	Ref.	- 2		4	S	9	۳		
	Remarks	⁵⁷ Fe ME, occupation: 8(f), 57%; 8(j), 43%; 8(i) 3%: critical ecconoment $R=0.775$, $H_{\perp}=12.4$ T	³⁷ Fe ME, ND		ND, atomic positions	point contact spectroscopy	²⁵⁷ Np ME		(1995) al. (1992) al. (1993)
aluminides	$P_{ m eff}$ $(\mu_{ m B})$			3.13				и и и	uski et al. rimmel et aydyuk et
ble 11c AnM ₅ Al ₇ :	0 (K)			-27					(4) S (5) K (6) N
Ta ary actinide	P_0 $(\mu_{ m B})$				1.2(1)				
Tern	$p_{ m s}$ $(\mu_{ m B})$	6.16/fu 0.814/Fe	1.23/Fe				1.3		
	T _{C,N} (K)	268 261	260		18(2)		250		
	magn. state	Гц.		Ъ.	\mathbf{AF}		ц		
	с ^а (пп)	0.5018		0.5145	0.5081				
	a ^a (nm)	0.8692		0.8728	0.8698(2)				al. (1985) et al. (1995 st al. (1994)
	x	Fe		Mn	Cu		Fe	RT.	<i>rences</i> Baran et Vagizov Halevy e
	An	_D					ď	^a At	Refe (1) 1 (2) 1 (3) 1

The $(R, An)Fe_5Al_7$ compounds seem to be the most mysterious group of materials among those being discussed in this review, and many experiments are still needed for further explanation of their properties.

3.2.1.3. (R, An) M_6Al_6 -type compounds.

3.2.1.3.1. M = Cr compounds. In table 12a (Felner et al. 1981b) we present the results of magnetic and ME investigations on compounds of Gd, Dy, Er and Lu. The Cr atom (ion) exhibits a local moment in ErCr_6Al_6 and not in GdCr_6Al_6 , although the Curie point of the latter compound is one order of magnitude higher than for other ferromagnets from this family of compounds. The magnetic structure of RCr_6Al_6 compounds is ferromagnetic, but a strong decline of the Curie point going from GdCr_6Al_6 ($T_C = 170 \text{ K}$) to DyCr_6Al_6 ($T_C = 20 \text{ K}$) and the low Curie constant of the latter compound might indicate strong CEF effects. Strangely enough, ME studies of ¹⁵⁵Gd (Felner et al. 1981b) at 77 K yield the pure quadrupole parameters. The hyperfine field direction is at an angle to the *c*-axis, which suggests that the magnetic structure is not necessarily simple. ME studies of ¹⁶¹Dy and ¹⁶⁶Er confirm magnetic ordering, and for DyCr_6Al_6 the hyperfine field has been determined.

3.2.1.3.2. M = Mn compounds. The results of magnetic and ME investigations for heavy lanthanides and Y are presented in table 12a according to Felner et al. (1981b). These results suggest that the Mn ion probably carries a local moment (~1.4 $\mu_{\rm B}$) as observed for YMn₆Al₆. However, since CEF reduces the rare-earth contribution to the effective moment, it is difficult to determine the Mn contribution, which seems to increase as the rare earths become heavier. In $GdMn_6Al_6$ there is no Mn contribution. The low Curie/Néel point is an indication of ordering in the lanthanide sublattice, but its character is unclear. On the one hand the paramagnetic temperature is negative, but on the other hand there are no maxima in the susceptibility curves. These facts, as well as the low value of the saturation moments, suggest a weak ferromagnetic (WF) structure. This last observation indicates that polarized conduction electrons contribute strongly to the magnetic properties of this class of materials. This idea is supported by the angle between the hyperfine field direction and the c-axis observed in ¹⁵⁵Gd ME (Felner et al. 1981b). The magnetic moment determined from the hyperfine field for GdMn₆Al₆ (1.3 μ_B) is a further confirmation of WF structure. The value of the hyperfine field for $DyMn_6Al_6$ is high, and likely also for $DyCr_6Al_6$ (Felner et al. 1981b). The Mössbauer spectra of compounds of Er and Yb are explained by spin-relaxation theory, and the observed spinrelaxation rates ($\sim 2 \times 10^9$ s⁻¹ for Er and 2×10^8 s⁻¹ for Yb) are slow. CEF effects are most probably the cause of these slow spin-relaxation rates (Felner et al. 1981b).

3.2.1.3.3. M = Fe compounds. The results of various types of physical examinations are listed in table 12b. These compounds also exist only for heavier lanthanides, Y and U. Compounds of magnetic lanthanides are ferrimagnetic (Felner et al. 1981a), whereas compounds of Y (Felner et al. 1981a) and U (Baran et al. 1985, Ptasiewicz-Bak et al. 1988) are ferromagnetic. ME studies on ¹⁵¹Eu and ¹⁷⁰Yb show that in EuFe₆Al₆ and YbFe₆Al₆ a mixed-valence state exists and moreover, that there is a strong admixture of EuAl₂ and YbAl₂, respectively (Felner et al. 1981a). ME on the ⁵⁷Fe nucleus revealed

	Ref.		I	-		-		1	1	1	-	1	7		
	Remarks	155 Gd ME	155 Gd ME	¹⁶¹ Dy ME	¹⁶¹ Dy ME		¹⁶⁶ Er ME				¹⁷⁰ Yb ME		Lattice parameters: $a = 0.8680$ nm, $c = 0.5134$ nm. C–W behavior above 100 K	a the Curie constant.	995)
luminides	φ ^a (°)	64(4) or 52(4)	83(5)											rmined fron	ski et al. (1
Table 12a 1)M ₆ Al ₆ -type a	H _{hf} (T)	16.8	20.4(5)	566.0(20)	556.0(20)									° Dete	(2) Su
ernary (R, Aı	$P_{ m eff}$ $(\mu_{ m B})$						1.4°			1.2°	1.2°	1.4°	4.35		
Ę	Ø (K)	158	6	ŝ	L	- T	4		-26	-18	-23	-44	-85		
	$P_{\rm s}$ $(\mu_{\rm B})$	5.5 ^b	1.1	1.9 ^b	2.1	5.1 ^b			0.3	1.9					
	T _{N,C} (K)	170(5)	15(2)	20(5)	6(2)	15(5)	2.6(1)		8(2)	2(1)				c-axis.	
	magn. state	ц	WF	F(?)	WF	щ	WF	D	WF	WF	Ч	ď	<u>م</u>	n H _h and .8 T.	. (1981b)
	W	ъ	Mn	Ç	Mn	ۍ ا	Mn	ŗ	Мn	Mn	Mn	Mn	Mn	e betwee 1 K in 1.	<i>nces</i> ner et al.
	R/An	PD		Dy		Er		Lu	đ	Tm	Yb	Y	n	^a Angl ^b At 4.	Referen (1) Fel

	Ref.		_	7	7	ŝ	4		4		4	5		9			1	1	6	6	ŝ	7	1	7	7	3	5			page
	Remarks		⁵⁷ Fe ME			o(T)	bulk, fast cooled	sample	powdered, fast	cooled sample	bulk sample	⁵⁷ Fe ME, magn.	structure disorder	mostly 8(f),	statistical occupation	of (i) and (i) ⁵⁷ Fe	⁵⁷ Fe ME	155 Gd ME		çd	$\mathfrak{I}(T)$		⁵⁷ Fe ME			$\mathfrak{I}(T)$	strong	magnetocrystalline	anisotropy	continued on next
	Ni ^b]	±2%	16				-		-		_	•					4	-				I	10				. 02	I		
	N _j ^b	土2%	17														26						30							
	$N_{\rm f}{}_{\rm p}$	±2%	67														60						60							
	¢ ª	2																43.4												
uminides	$H_{ m hf}$ at 4.2 K	E																20.9(2)												
-type alı	$p_{ m eff}^{({ m R})}$	ALL .															8.0		7.94 ^d	7.94			9.2	9.72						
An)Fe ₆ Al ₆	$p_{ m eff}^{ m (Fe)}$	±0.2	3.0	3.42 ^d													3.3		3.5 ^d	3.25			3.1	3.37	3.99					
ary (R, A	<i>0</i> (¥	± 2	327	375 ^d			360										328		50 ^d	115			328	160 ^g	260 ^d					
Tern	H_{c}											0.002															0.3 °			
	$P_{s}^{(\mu_{c})}$	(8-1)					8.40°					5.1°															0.77°			
	${}^{T_{\max}}_{(K)}$	±10	250				260				266°						220						260							
	$T_{\rm CN}$	±5	345			320	308	i V	262		238	265					345		350		328		335	330		334	310			
	magn. state		ы											Ч			Æ						Fi				Æ			
	(uu)		.4992).5036°	.5018												5015		.501 ^f			.500	.5029	.5027						
	a (mn)		0.8646 (0.8712° (0.8732 (0.8687 (0.869 ^f (0.864 (0.8651 (0.8641 (
	R/U		Υ														Gd						Tb							

W. SUSKI

Table 12b

Ref.		1	1	7	Э	4	-	4			`	9	9			1	7		ŝ	4				Ś	-	1	7	7	÷	5	t page
Remarks		⁵⁷ Fe ME	161 Dy ME	no CW behaviour	$\rho(T)$	powdered, fast	cooled sample	bulk, fast cooled	sample, ac suscept.,	magnetostriction	$\lambda(H,T)$		Fe atoms prefer (f)	and (j) sites; ⁵⁷ Fe	ME	⁵⁷ Fe ME		ĺ	$\rho(T)$	bulk, fast cooled	sample, $\chi_{\rm ac}(T)$,	magnetostriction	$\lambda(T,H)$		⁵⁷ Fe ME	166 Er ME			$\rho(T)$		continued on nex
$N_i^{\ p}$	土2%	5														ŝ									-						
N_{j}^{b}	土2%	32														35									30						
$N_{\rm f}^{\rm \ b}$	土2%	63														61									99						
т ө б	2																														
	at 4.4 N																									824(2)					
$P_{\rm eff}^{(\rm R)}$	(µB)	9.5														9.8	10.4 ^d								9.2		9.59				
$P_{\rm eff}^{({\rm Fe})}$	(MB) 土0.2	3.0														2.7	3.2 ^d	°UC.C							3.1		3.29 ^d	4.048			
0	£5	230						310								311	309 ^d	°C67							328		385 ^d	4088			
H_{c}												0.25 ^e												0.06°						0.02 °	
 $P_{\rm s}$	(µ ^B)					1.47°						1.12°	1.2°							1.32°				1.32°						3.39°	
T_{\max}	2) 1	250				260										215				230					210						
$T_{\rm CN}$	£€	325			336	331	!	347				311	311			310	340		341	302				302	320		330		343	304	
magn.	state	Æ		Æ												Ē									Ē						
0		0.5001		0.5026												0.4985	0.5023								0.5016		0.5021				
a	(IIII)	0.8650		0.8642												0.8636	0.8625								0.8619		0.8611				
R/U		Dy														Но									Er						

Table 12b, continued

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES

	Ref.		×	9 6 11 10 8 10 8 10 8 10 8 10 8 10 8 10 8 1		
	Remarks	⁵⁷ Fe NE MV, contained EuAl ₂ ¹⁵¹ Eu ME	MV, contained YbAJ ₅ ⁵⁷ Fe ME ¹⁷⁰ Yb ME	ND ⁵⁷ Ĥe ME	al phase.	
	N _i ^b ±2%	7	6	٢	etragon	
	N _j ⁵ ±2%	31	30	35	T.	()
	N _f ^b ±2%	62	61	58	nt of a s of 0.128	al. (198 1. (1988 5)
	\$ (0)		44(2)		ll amoui c field c	Wang et (1983) (1985) 3ak et a al. (1995
q	H _{hf} at 4.2 K (T)	24.0(5)	99.0(3)		tained sma er magneti 00 K.	an-zhong V rran et al. (rran et al. (tasiewicz-I tagizov et s 'agizov et s
ontinue	$p_{ m eff}^{(m R)}$ $(\mu_{ m B})$				^f Cont ^g Und ^h P_0 . ⁱ At 3	(7) Xi (8) Ba (9) Ba (9) Ba (10) P (11) V
e 12b, c	$\stackrel{p_{ m eff}}{(\mu_{ m B})}_{\pm 0.2}$	7.6	6 69)hi		
Tabi	⊕ ±5	3.1		2.1(4		
	H _c (T)	345	101			
	$p_{ m s} \ (\mu_{ m B})$			6.84/fi 3.2(5) 0.917 ¹		
	${T_{\mathrm{max}} \over (\mathrm{K})} \pm 10$	150	120			8)
	${}^{T}_{\mathrm{CN}}_{\mathrm{CN}}$ ± 5	320 135	210	355 355 350	iis. 32 T.	ka (198
	magn. state	E i	E H		und <i>c</i> -ax s. 1 of 0.3	a) (1988) nełkows 0)
	с (nm)	0.5005 0.5160	0.4987		en H _{hr} ⁶ f Fe site nple. stic field	l. (1981: a et al i and Cl al. (1990) l. (1980)
	a (nm)	0.8605 0.8937	0.8638		gle betwee ulation of nealed sar ier magne 30 K.	<i>ences</i> elner et al hełkowsk hełkowsk ilonek et a vpiel et al vpiel et al
	R/U	E E E	۲۵ ۲۵	>	^a Ang ^b Pop ^c Anr ^d Unc ^e At 8	Refer (1) Fi (2) C (3) C (4) Je (5) P (6) P (6) P

that the Fe atom predominantly occupies the 8(f) position, with a second preference for the 8(j) site (Felner et al. 1981a). The same has been reported by Vagizov et al. (1995) for UFe₆Al₆. Only for YbFe₆Al₆ are the 8(j) and 8(i) positions reported to be statistically occupied (Felner et al. 1981a, Popiel et al. 1989). For this compound magnetic structure disorder was observed (Popiel et al. 1989, 1990).

Apart from dc magnetic susceptibility and ME for these compounds, examinations have been reported of electric resistivity (Chełkowski and Chełkowska 1988) and ac magnetic susceptibility and magnetostriction (Jelonek et al. 1990). Some of these experiments revealed a strong influence of thermal history and the form of the sample on the physical properties. These differences are particularly pronounced for the compounds of Tb, Ho and Er (Chełkowska et al. 1988). The general feature of the temperature dependences of magnetization are: maxima at temperatures close to ~220 K, lack of saturation for the majority of compounds, and a small value the of saturation moment at lower temperature. The Curie points determined by means of ME examinations are close to 320-350 K (except for EuFe₆Al₆ and YbFe₆Al₆, see Felner et al. 1981a, Chełkowski and Chełkowska 1988). UFe₆Al₆ exhibits a similar value for $T_{\rm C}$ (355 K), (Baran et al. 1985, Ptasiewicz-Bak et al. 1988, Vagizov et al. 1995). This fact indicates a lack of difference between the compounds of magnetic and nonmagnetic f-electron elements and makes it difficult to determine the contribution of the f-electron element to magnetism from magnetic measurements alone. Even ND experiments performed on UFe₆Al₆ (Ptasiewicz-Bak et al. 1988) cannot give any final conclusions, due to the rather limited accuracy of the results, regarding the contribution of the uranium atom to the magnetic order.

3.2.1.3.4. M = Cu compounds. The data obtained in magnetic and ME investigations are collected in table 12c. Felner et al. 1981b claim that the slope of the magnetization curves as well as the negative value of Θ suggest that the RCu₆Al₆ compounds (where R are heavy lanthanides) order antiferromagnetically due to R-R exchange, and that this is confirmed by the low Néel temperature. However, the maximum in the M(T) curve is diffuse and ¹⁵⁵Gd ME examination reveals an angle between the hyperfine field direction and *c*-axis for GdCu₆Al₆ (Felner et al. 1981a). Moreover, ME on ¹⁶¹Dy in DyCu₆Al₆ does not show any magnetic ordering (Felner et al. 1981a). Therefore, the conclusion about AF ordering in these materials is on a weak footing and still needs confirmation by neutron diffraction. Diamagnetic properties of YbCu₆Al₆ and ¹⁷⁰Yb ME prove that the Yb ion is divalent in this compound.

3.2.1.3.5. The aluminides with other elements. Up to now two such compounds and their properties have been reported: $CeAg_4Al_8$ (Rauchschwalbe et al. 1985), which is neither magnetic nor superconducting; and $GdRh_6Al_6$ (table 12d), which is ferromagnetic below 30 K (Felner et al. 1981a,b) with an angle between the hyperfine field direction and the *c*-axis as determined in ¹⁵⁵Gd ME (Felner et al. 1981b).

3.2.1.4. $(R, An)Fe_xAl_{12-x}$ solid solutions. As mentioned above, it appears that for the majority of the discussed materials solid solutions exist over a broad concentration range; the most systematic study has been carried out for iron as the transition metal. Previously, the UCu_{4+x}Al_{8-x} system has been described and the existence of the UMn_{4+x}Al_{8-x} alloys

							Terna	T uy RCu	able 12c ₆ Al ₆ -type aluminides	
Я	a (nm)	<i>с</i> (пп)	magn. state	$T_{\rm C,N}$ (K)	Θ (T), ± 5	$p_{ m eff}$ $(\mu_{ m B})$	H_{hf} (T)	¢ a	Remarks	Ref.
Gd	0.8691	0.5062	AF	21(2)	-22(1)	7.9(1)	24.6(2)	48(3) 61(3)	155 Gd ME	1
Tb			AF	33.4(1)	-54					2
Dy	0.8662	0.5042	AF(?)	3.9(1)	-14(1)	10.9(1)			¹⁶¹ Dy ME; not ordered ?	1
Но			AF	1.9(1)	-11					2
Er	0.8630	0.5029	AF	2.6(1)	-12(1)	9.9(1)			¹⁶⁶ Er ME, isomer shift, spin-relaxation theory	1
Tm	0.8624	0.5040	Ч		-5(1)	7.3(1)				1
				3.9(1)	-5					2
Υb			D						¹⁷⁰ Yb ME, isomer shift, Yb ²	+ 2
Гſ			Ω							2
^a An	gle betw	/een H _{hf}	and c-i	axis.						
D of a .	00000									

References (1) Felner et al. (1981a)

(2) Felner et al. (1981b)

					Terna	Tal try RRh ₆ .	ble 12d Al ₆ -type a	luminide		
R	a (nm)	с (nm)	magn. state	<i>Т</i> _с (К)	Θ (K) ±5	$p_{ m s}$ ($\mu_{ m B}/{ m fu}$)	H _{hf} (T)	ø ª (°)	Remarks	Ref.
Gd			F	30(2)	47	4.2	18.6(4)	60(2)	at 4.1 K, under 1.8 T ¹⁵⁵ Gd ME	1 2

(2) Felner et al. (1981a)

^a Angle between $H_{\rm hf}$ and *c*-axis.

References

(1) Felner et al. (1981b)





tion x (Xian-zhong Wang et al. 1988).

is known (Suski et al. 1995). Below we are going to describe the properties of the $(R, An)Fe_xAl_{12-x}$ systems, where R = Gd, Tb, Er and Y and An = U. The existence range differs for the various f-electron metals.

For Gd compounds Xian-zhong Wang et al. (1988) reported that in addition to the materials previously obtained (and described) in this system, species with x=8 and 10 exist, and these were prepared by melt spinning. Unfortunately, these samples contain an amount of free α -Fe. Similar results have been obtained for R=Dy (Xian-zhong Wang et al. 1988). In fig. 15 (Xian-zhong Wang et al. 1988) the Curie points of the GdFe_xAl_{12-x} alloys are plotted versus Fe concentration x. One can see that the extrapolated T_C for the ideal GdFe₁₂ would be about 600 K, but T_C for x=10 is already interesting from the



Fig. 16. Distribution of the Fe atoms in 8(f) site (upper panel) and 8(i) + 8(j) sites (lower panel) versus x in the RFe_xAl_{12-x} alloys, determined by ⁵⁷Fe ME examination: circles, R=Gd (Liu et al. 1987); squares, R=Er (Kamimori et al. 1988); triangles, R=Y (Felner and Nowik 1986b).

applications point of view. The saturation magnetizations at 300 K are 6.07 and $10.6\mu_{\rm B}/{\rm fu}$ for x = 8 and x = 10, respectively, which is considerably lower than those for compounds of Si, V, Ti, etc. The average Fe moment at room temperature deduced from the average hyperfine field (⁵⁷Fe ME) amounts to $1.5\mu_B$. Therefore, the deduced Gd moment for x = 10is $4.5\mu_{\rm B}$, assuming a ferrimagnetic structure in which the Gd sublattice is antiparallel to the iron sublattices. The fit to the Mössbauer spectrum of GdFe₁₀Al₂ shows that the 8(i) and 8(f) sites are fully occupied by iron, while the 8(j) site is equally occupied by Fe and Al. Figure 16 demonstrates the site occupancy of Fe atoms for alloys with $x \leq 6$ for R=Gd (Liu et al. 1987), R=Er (Kamimori et al. 1988) and R=Y (Felner and Nowik 1986b). As was shown before for x=4, the 8(f) site is completely filled with Fe atoms for R=Gd but not for R=Er and Y. For x=6, 60% of the Fe atoms remain at 8(f) for R=Gd, but only 33% for R=Er and almost no Fe atoms for R=Y. These facts show that occupancy of the 8(f) site by Fe atoms strongly depends on the R atom, and the number of Fe atoms at the 8(f) site decreases remarkably as x increases. The last tendency is also observed in the $TbFe_xAl_{12-x}$ system (Felner and Nowik 1988) where the occupation of 8(f) sites by Fe atoms amounts to zero as shown in fig. 17. The contribution of the Tb sublattice to the magnetization and associated



Fig. 17. Distribution of the Fe atoms in individual crystallographic positions in $\text{TbFe}_x\text{Al}_{12-x}$ alloys versus Fe concentration, *x*, as determined by ⁵⁷Fe ME examination (Felner and Nowik 1988).

high magnetic anisotropy and the SG structure below a relatively high T_c lead to a wide variety on unusual phenomena. This includes observed negative magnetization, wide hysteresis loops and double-peaked magnetization-temperature curves which are the results of high magnetic anisotropy with a step temperature dependence of the rare-earth sublattice.

The magnetic properties of the $\text{ErFe}_x \text{Al}_{12-x}$ system obtained from measurements of the temperature dependence of the ac susceptibility are presented in fig. 18. At x = 4 the magnetic couplings of Er-Er and Fe-Fe are ferromagnetic; Er-Fe is antiferromagnetic below T_{C1} (AF in fig. 18) and Fe-Fe is AF between T_{C1} and T_N (A in fig. 18) (Felner and Nowik 1978, Felner et al. 1983). Another transition T_{C2} was observed at x=4.25 and x=4.5. Small spontaneous magnetization and large high-field susceptibility were observed between T_{C1} and T_{C2} (FR', fig. 18). In this phase ferromagnetic clusters may exist in the AF matrix. One can see that the FR region expands with increasing x. This is due to the increment of the Fe(f)-Fe(i,j) and Fe(i,j)-Fe(i,j) pairs and decrement of the Fe(f)-Fe(f) pairs. Therefore, Fe(f)-Fe(i,j) and Fe(i,j)-Fe(i,j) couplings are assumed to be ferromagnetic. The magnetic coupling of Fe(f)-Fe(f) is AF at x=4. The above-mentioned W. SUSKI



Fig. 18. Magnetic phase diagram (T, x) of the ErFe_xAl_{12-x} alloys determined by the measurements of ac susceptibility (Kamimori et al. 1988). The symbols are explained in the text.

ferromagnetic cluster is considered as a mixed state of AF coupling of Fe–Fe pairs at x=4 and ferromagnetic above x=4.75.

A transition from ferrimagnetism to spin-glass (SG) behavior has been reported by Felner and Nowik (1986a,b) for YFe_xAl_{12-x} and $4 \le x \le 6$. As mentioned in previous paragraphs, YFe₄Al₈ is an antiferromagnet and YFe₆Al₆ is ferrimagnetic, whereas the alloys with x=4.5, 5.0 and 5.5 exhibit phenomena associated with SG behavior below $T_{\rm C}$, yet they order ferrimagnetically at a higher temperature as evidenced by the ⁵⁷Fe Mössbauer spectra. Both temperatures are shown in fig. 19a, while fig. 19b demonstrates the occupation of the crystallographic sites by the Fe atoms. This is in fair agreement with fig. 17, but additionally the occupancy of the 8(i) and 8(j) positions is shown separately in fig. 19. In the SG state large field-cooled (FC) and zerofield-cooled (ZFC) remanences are observed and the remanent magnetization is time dependent. The magnetization curves strongly depend on cooling rates and the hysteresis loops have unusual slopes. The SG transition temperature $T_{\rm SG}$ decreases as the external magnetic field increases, accurately following a "2/3 power law".

Among the actinides only the UFe_xAl_{12-x} system has been investigated over a broad composition range. In fig. 20 we present the saturation magnetization, magnetic moment of the iron sublattice and Néel/Curie points of these alloys for Fe concentration $3 \le x \le 6$ (Vagizov et al. 1995). One should note that the Curie point of 478 K for x = 8 reported by Zeleny et al. (1991) is also roughly located on the $T_{\rm C}(x)$ curve. This curve is linear and can be used as a characteristic of the concentration. On the contrary, a plot of the saturation magnetization $M_{\rm s}$ vs. x exhibits pronounced a minimum for x = 4. The value of $M_{\rm s}$ observed at this concentration is the value of the magnetic moment of the uranium



Fig. 19. (a) Curie/Néel points, $T_{C,N}$ (circles) and the temperature of transition to SG state, T_{SG} (diamonds). (b) Distribution of Fe atoms in the following crystallographic positions: 8(f), circles; 8(i), triangles; 8(j), squares, versus Fe concentration x in YFe_xAl_{12-x} alloys (Felner and Nowik 1986b).

Fig. 20. Saturation magnetization, M_s (circles) at 4.2 K, magnetic moments of the Fe sublattice (triangles) and ordering temperature $T_{C,N}$ (crosses) versus Fe concentration x in UFe_xAl_{12-x} alloys (Vagizov et al. 1995). The diamond corresponds to the neutron diffraction data (Gal et al. 1990).

sublattice $(\sim 1\mu_B)$ and is close to the value of the uranium magnetic moment determined in a neutron-diffraction experiment reported by Gal et al. (1990). For the understanding of this statement we should remind ourselves that the magnetic structure of this material

consists of an AF iron sublattice and a ferromagnetic uranium sublattice (see Paixão et al. 1994).

The jump for $x \approx 4.2-4.4$ corresponds to the transition from the AF to the ferri- or ferromagnetic state. As has been shown by ME experiments this jump is related to the Fe atoms beginning to enter into 8(j) crystallographic positions. Andreev et al. (1992a) claim that with the increasing x and consequently increasing number of Fe atoms at the 8(i) sites, the uniaxial contribution to the anisotropy becomes larger, leading to a decrease of the total anisotropy. The increase of M_s for x < 4 results from noncompensated AF structure of the Fe sublattice. ⁵⁷Fe ME experiments (Vagizov et al. 1995) show that as x increases above x=4 only few Fe atoms enter the 8(i) sites and there is only a tiny difference in occupation of two other positions for x=5 and 6. This observation cannot explain the apparent increase of the Curie point from x=5 to x=6. However, the total Fe magnetic moment increases linearly with x. The observed asymmetry in the ME spectrum of UFe5Al7 at RT might be related to a small admixture of Fe-Al nonmagnetic alloy (Gal and Halevy, private communication). The Curie point of this compound is confirmed by the results of Halevy et al. (1994) who reported $T_{\rm C} = 250 \,\rm K$ for NpFe₅Al₇. 237 Np ME for this compound gives the hyperfine field at 4.2 K amounting to 286(10) T, which corresponds to a magnetic moment of $\sim 1.3 \mu_{\rm B}$.

3.2.2. Gallides

ThMn₁₂-type gallides have been reported only for the rare earths (Weitzer et al. 1990, Burzo et al. 1992, Morariu et al. 1993, Rogalski et al. 1993). Weitzer et al. (1990) claimed that the RFe_xGa_{12-x} alloys exist with $x \approx 6$ and that for heavier lanthanides the ThMn₁₂type structure is stable only at higher temperatures. The temperature range of existence of these materials is shown in fig. 21a. From this figure it follows that for heavier lanthanides LT modification exhibits orthorhombic ScFe₆Ga₆-type (Immm) structure (Weitzer et al. 1990). In turn, the chemical cell volume (fig. 21b) yields a smooth curve, except for that of Ce and Yb gallides; this can suggest a mixed-valence state of Ce in this alloy. However, the Yb point falls below the line for unknown reasons. Both crystallographic modifications do not exhibit a difference in the volume of chemical cell.

The lattice parameters and magnetic data of these materials are presented in table 13. They exhibit ferromagnetic character below $T_{\rm C} = 560$ K (for Lu compound at maximum) and 340 K (for Pr compound at minimum) at which all magnetic sublattices order simultaneously. The compounds of light lanthanides are considered to be collinear or canted ferromagnets, and the magnetization vector is supposed to be close to the *a*-*b* plane. In addition, strong hysteresis effects are visible in all alloys. Energy products are the highest for (Pr, Sm)Fe_{~6}Ga_{~6}. Ferrimagnetic behavior is observed for the heavy-rare-earth compounds and both Fe and R sublattices couple antiparallel, exhibiting easy-plane anisotropy. Magnetic properties are apparently not related to the crystallographic modification of these materials. In turn, Burzo et al. (1992) have reported the existence of gallides for Gd and Y with concentrations $10 \le x \le 11$. Therefore, these materials should be discussed in subsequent sections but for the sake of simplicity we will present them here.



Fig. 21. (a) Temperature range in which RFe₆Ga₆ compounds exist for the two structural modifications with the ThMn₁₂and ScFe₆Ga₆-type structures. The region of coexistence of the two structure types may approximately be located within the limits $1.2 < r_{\rm R}/r_{\rm (Fe, Ga)} < 1.4$ (r_i are the metal radii); (b) volume of chemical cell (Weitzer et al. 1990).

The magnetic properties are presented in fig. 22 and in table 13. It follows from fig. 22 that when the Fe atom is substituted by the Ga atom the Curie points increase while the saturation magnetization and anisotropy fields decrease and the easy axis of magnetization is the *c*-axis. Since Gd is in the *S*-state and Y is nonmagnetic the anisotropy is mainly determined by the iron sublattices. Assuming that the Gd moment amounts to $7\mu_B$, the average iron moments were determined as shown in fig. 22c (M_{Fe}). The difference between M_{Fe} for Gd and Y compounds shows the contribution of the induced iron moment resulting from the presence of the magnetic lanthanide. Extrapolation of M_s to x=0 determined from magnetic measurements gives $1.96\mu_B/Fe$ atom for the Y alloy and $2.10\mu_B/Fe$ atom for the Gd alloy (Burzo et al. 1992), while ⁵⁷Fe Mössbauer effect provides 2.15 and $2.31\mu_B/Fe$ atom for the Y and Gd alloys, respectively (Morariu et al. 1993). Both these last values are about 10% larger than those determined by Burzo et al. (1992). Contrary to these reports, Cadogan et al. (1993) have observed for the YFe_{12-x}Ga_x system with $1 \le x \le 2$ the formation of either hexagonal Th₂Ni₁₇ or rhombohedral Th₂Zn₁₇ structures plus α -Fe(Ga).

In order to improve the magnetic properties, Fe was substituted by Co in the Pr compound (Weitzer et al. 1990). However, this substitution markedly diminishes M_s and T_c , and therefore we will not devote more space to these alloys.

	Ref.	-	1	2	2	7	3,4	1	Ч	-	-	1	1	-	7	7	7	3,4	1	1	1	1	1	1	page
							stributed over (j)											/ distributed over							ontinued on next
	Remarks			see fig. 21	anisotropy field	anisotropy field	Ga atoms randomly dis and (f) sites		'mischmetal'							see fig. 21		Ga atoms are randomly (i) and (f) sites							0
	$(BH)_{max}$ (kJ/m ³)									15	4	15													
s	T _c (K)	500	350					380	340	370	430	490	510	510					475	475	520	450	490	500	
e gallide	<i>Н</i> _е (Т)	<0.05	0.02					0.01	0.02	0.17	0.09	0.28	0.03	0.05											
Table 13 e _x Ga _{12-x} -typ	M ^M ^r (Am ² /kg)	8	£					2	5	44.4	21.6	27.0	2.8	6.0					0.1	0.2	0.8	0.1	0.7	1.1	
emary RI	$p_{\rm s}$ $(\mu_{\rm B}/{ m fu})$	8.6	3.9		1.89 ^b	1.98		9.3	8.3	9.3	10.8	6.2	3.6	3.1	1.94 ^b	2.03 ^b	2.11 ^b		0.8	0.7	0.8	0.8	1.6	2.0	
Т	c (nm)	0.50773(23)	0.86707(54)					0.50859(27)	0.50996(25)	0.51006(17)	0.50992(22)	0.50884(51)	0.50933(24)	0.86775(52)					0.50806(24)	0.86642(47)	0.50755(20)	0.86674(70)	0.50759(16)	0.86440(42)	
	<i>b</i> (mn)		0.85438(27)											0.85761(64)						0.85808(55)		0.85307(70)		0.85213(30)	
	a (mn)	0.85958(22)	0.50715(22)					0.86873(22)	0.87442(16)	0.87173(10)	0.86831(12)	0.86350(22)	0.86308(24)	0.50786(10)					0.86197(17)	0.50798(18)	0.85902(13)	0.50647(15)	0.85940(11)	0.50598(14)	
	Str. type ^a	-	П	-	I	Ι		Ι	I	Ι	Ι	Ι	1	Π	I	Ι	Ι		I	Π	Ι	II	I	II	
	×	6		10	10.5	11.0		5.4	5.4	5.5	5.9	5.8	5.8	5.8	10.0	10.5	11.0		5.8		5.9		5.9		
	×	۲						Ce	MM	Pr	ΡN	Sm	Gd						đT		Dy		Но		

204

W. SUSKI

						Tabl	e 13, contin	ted				
2	x	Str. tyme ^a	a (mm)	(uu)	ر (۱۱۱۱)	$P_{\rm s}$ (m./fii)	M ^M (Am ² /kg)	ц,	r _c	(BH) _{max} Ret (kJ/m ³)	narks	Ref.
		246		(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		(nr flad)		E				-
Ъ	5.8	I	0.85930(16)		0.50742(23)	C. Z	1.0		480			-
		Π	0.50690(13)	0.85461(40)	0.86607(56)	2.0	0.4		420			1
Tm	5.8	Ι	0.85839(19)		0.50739(18)	4.6	11.0	0.05	460			1
		Π	0.50619(18)	0.85267(57)	0.86605(67)	3.6	4.8	0.02	470			1
Υb	5.8	Π	0.50450(19)	0.84982(48)	0.86441(59)	5.3	0.6		530			1
Ľu	5.8	Ι	0.85548(17)		0.50619(8)	10.6	1.6		540			1
		Π	0.50488(17)	0.84909(81)	0.86531(75)	2.5			560			-
^a Stru ^b Per	cture ty Fe atom	pe: I, T 1 in the	hMn ₁₂ ; II, ScH 8(i) position, e	Pe6Ga6. calculated from	m H _h determi	ned in ⁵⁷ I	e ME expen	iment.				
Refer	nces	01/10					Ð	Morarin	et al (1003)		

kejerences (1) Weitzer et al. (1990) (2) Burzo et al. (1992)

(3) Morariu et al. (1993)(4) Rogalski et al. (1993)

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES



Fig. 22. (a) Curie points, $T_{\rm C}$, (b) spontaneous magnetization, (c) Fe moment determined at 4.2 K, $M_{\rm Fe}$, (d) anisotropy field $H_{\rm A}$, at 77 K (circles) and 300 K (triangles), versus Fe concentration x in GdFe_xGa_{12-x} (open symbols) and YFe_xGa_{12-x} (solid symbols) (Burzo et al. 1992).

One should also note that for expected technical application an alloy has been studied in which 'mischmetal' is utilized instead of a pure rare-earth element (Weitzer et al. 1990). (The nominal composition of 'mischmetal' is about 50% Ce, 30% La, 16% Nd and 4% Pr; it can vary somewhat depending upon the ore source but the relative amounts $Ce \gg La \gg Nd > Pr$ always hold). It follows from table 13 that the 'mischmetal' alloy behaves more like CeFe_{5.4}Ga_{6.6} than like PrFe_{5.5}Ga_{6.5}, so that it does not have particularly favorable magnetic parameters. Therefore, in spite of its relative low price, this alloy cannot be recommended as a new magnetic material.

Finally, it is noted that gallides also exist in the Dy–Co–Ga and Yb–Co–Ga systems (see Gladyshevsky et al. 1990), and that In compounds of the LnAg_{5.4}In_{6.6}-type have been reported (Sysa 1991), although their properties have not been investigated.

3.3. Compounds of the rare earths with high concentration of transition elements

The rare-earth compounds and the actinide compounds will now be treated separately, in the present sect. 3.3 and in sect. 3.4, respectively. The reasons are that: (1) the rare-earth compounds form a huge class of materials, much bigger than that of the

actinides, with a vast amount of information available, and (2) the research on these materials was apparently motivated by their potential commercial applications. In fact, the high Curie points and magnetizations justified the interest in these alloys as useful for some technological purposes; sometimes they are superior to the Nd–Fe–B derivatives. However, their remanence and coercivity are rather low and the desire to improve these parameters motivated much of this extensive research. Below, particular attention will be devoted to the following topics: bulk magnetic properties of polycrystals, single crystals and thin films; anisotropy; spin-reorientation transition temperature; theoretical attempts to explain observed behavior; and finally technological processes proposed for improving magnetic parameters.

3.3.1. Bulk magnetic properties of the rare-earth compounds

The bulk magnetic properties of the compounds with Fe, Co and Ni as transition elements, and with Si, Ti, V, Cr, Mn, Mo, W, and Re as structure-stabilizing components, will be discussed. The pseudoternaries will also be presented because a substitution of one component by another may improve materials parameters.

Generally, among the compounds presented only a small number contain La, Ce, Eu, Yb or Lu; one can assume that many possible compounds with these elements were not synthesized because of their apparently weak magnetic character. On the other hand, Y compounds are frequently investigated not only because these materials are convenient standards for the lanthanide compounds (because the magnetism is located only in the transition-metal sublattice), but also because some of these alloys exhibit reasonable magnetic behavior. The best magnetic parameters seem to indicate that compounds containing Ti and V as stabilizing elements are better than those utilizing the 4d and 5d elements. This observation can be related to the crystallographic position occupied by the stabilizing component, e.g., Mo seems to substitute Fe in the 8(i) position and this substitution decreases the Curie point relative to compounds with other stabilizing elements (see e.g. Ermolenko et al. 1990). Frequently, the composition of these alloys, $RM_{12-x}T_x$, does not correspond to the stoichiometry with x=2, and the index of the stabilizing component is usually $1 \le x \le 3$. In order to obtain more favorable magnetic parameters the whole existence range is investigated and the best results are obtained for different values of x.

Almost all of these compounds exhibit an admixture of α -Fe, which surely improves magnetic parameters, but makes it difficult to determine precise intrinsic numerical values.

3.3.1.1. Compounds with Si. Compounds with Si are obtained with Fe and Ni, and with Fe partially substituted by Co (Buschow 1988a, Solzi et al. 1990); however, pure compounds with Co do not exist. The silicides are one of the few groups exhibiting the stoichiometry $RFe_{10}Si_2$. Their properties are collected in table 14. In this family $PrFe_{10}Si_2$ is exceptional because it has a cubic, $NaZn_{13}$ -type of structure (Sakurada et al. 1992). The magnetic moments of $YFe_{10}Si_2$ and $LuFe_{10}Si_2$ are close to each other, $M_s = 18.3\mu_B/fu$
						•			
2	X	a	c	$T_{\rm C}$	$M_{\rm s}$	H_{a}	$H_{ m hf}$	Remarks	Ref.
		(um)	(uu)	(K)	$(\mu_{\rm B}/{\rm fu})$	E	E		
Υ	Ъе	0.8313	0.4737	530				CEF parameter $A_2^0 = -120 \text{ K}/a_0^2$, easy axis	Ч
		0.83988	0.47523	543	14.04 ^b				7
		0.8426	0.4756	569	18.26 ^a	2.2 ^ª			ε
Ł	Fe							NaZh ₁₃ -structure	4
PZ	Fe	0.8464	0.4771	574	15.1°	1.7°		CEF parameters, ⁵⁷ Fe ME, site occupation	S.
				570				$T_{\rm SR} = 120 {\rm K}$	9
Sm	Fe	0.84671	0.47548	606					7
								high field magnetisation	8
		0.8449	0.4753	590	15.29°	~0.52		oriented powder, atomic parameters	6
							28.9°	⁵⁷ Fe ME	10
							27.0 ^d		10
g	Fe	0.8436	0.4757	610			24.6 ^b	⁵⁷ Fe ME, easy axis, CEF parameter $A_2^0 = -120 \text{ K}/a_0^2$	1,11
		0.8437	0.4757	610				CEF parameter $A_2^0 = -123 \text{ K}/a_0^2$	12
							25.6 ^d	⁵⁷ Fe ME	13
		0.8444	0.4761	623	11.88ª	0.43ª			e
Ъ	Fe	0.8409	0.4748	593	10.25 ^a			$T_{\rm SR} = 202, 430 {\rm K}$	£
				570				⁵⁷ Fe ME, CEF parameters, site occupation, oriented sample,	9
								$T_{\rm SR} = 170 {\rm K}$	
	ž							INS, transition at about 6 meV, unresolved	14
Dy	Fe	0.8413	0.4753	573	9.73ª	3.4ª		$T_{\rm SR} = 127, \ 177 {\rm K}$	ŝ
,				540				57 Fe ME, CEF parameters, site occupation, oriented sample,	9
								$T_{\rm SR} = 200 \rm K$	
		0.8479	0.4767	575			28.1 °	57 Fe ME, $T_{SR} = 210 \text{ K}$	15
				613(1)			48 ^b	¹⁶¹ Dy ME, $T_{\text{SR}} = 228(3)$ K	16
Но	Fe	0.8411	0.4759	566	10.04 ^a	2.7ª		$T_{\rm SR} = 21 {\rm K}$	ŝ
				525				⁵⁷ Fe ME, CEF parameters, site occupation, oriented sample,	9
								$T_{\rm SR} = 60 {\rm K}$	
	ïŻ							INS, transition at about 6 meV, unresolved	14
								continued on ne	xt page

Table 14 Ternary RM₁₀Si₂-type silicides

R M	a (mn)	с (um)	<i>T</i> _c (K)	$M_{ m s}$ ($\mu_{ m B}/{ m fu}$)	H _a (T)	$\stackrel{H_{\mathrm{hf}}}{(\mathrm{T})}$	Remarks		Ref.
Er Fe	0.8384	0.4747	559 505	10.77ª	3.4ª		$T_{\rm SR} = 19 {\rm K}$ $T_{\rm SR} = 48 {\rm K}$, CEF parameters ${}^{57}{\rm Fe} {\rm ME}$, CEF parameters, site $T_{\rm SR} = 65 {\rm K}$	occupation, oriented sample,	3 17 6
Ņ				18.3 ^b		27.1 ^b 26.6 ^c	⁵⁷ Fe ME INS, CEF levels at 2.5, 3.3, 4.0), 4.6, 5.0, 5.8 and 6.2 meV.	18 18 18
Tm Fe				15.5 ^b		702(4) ^b 22.2 ^b	doublet ground state ¹⁶⁹ Tm ME ⁵⁷ Fe ME		16 16
* Fe Lu Fe	f(y) 0.8380	f(y) 0.4755	f(y) 548	18.37ª	2.1ª	f(y)	$(Tm_{y}Dy_{1-y})Fe_{10}Si_{2}$: ⁵⁷ Fe ME		19 3
Y Co			760	11.5ª		26.7°	⁵⁷ Fe ME ND, angle of moment direction	with c -axis = 30°	18 20
* * 4							$\begin{array}{l} Y(Fe_{1-x}Co_{x})_{10}Si_{2}; \ x \leqslant 0.3; \ ND \\ Y(Fe_{1-x}Co_{x})_{10}Si_{2}; \ x \leqslant 0.5 \\ \text{Dress}, \ x \leqslant 0.5 \end{array}$		20 21
sm *	0.820843(3)	0.467155(3)					IND, atomic background ND, atomic parameters Sm(Fe,Co) _{12-x} Si ₂		14 23 22
* Variable ^a At 1.5 K	composition; see Rei	marks column.	ں عر	At 4.2 K. At 77 K.			^d At 298 K. ^e At 293 K.		
Referenco (1) de Mo (2) Ge et (3) Q. Li (4) Sakura (5) Chin e (6) Christů	es ouj and Buschow (199 al. (1992) et al. (1991) uda et al. (1992) at al. (1991a) des et al. (1991a)	88) (7) 1 (8) (8) (9) ((10) (10) (11) (12) (12)	Buschow (1 Kaneko et a Ohashi et al Ding and I Buschow e Ermolenko	988a) dl. (1989) l. (1988a) Rosenberg (1 21 al. (1988) e et al. (1990)	(4066	(13) 5 (14) N (15) N (15) N (16) C (17) S (17) S (18) S	Sinnemann et al. (1989b) Moze et al. (1992) Va et al. (1991) Jubbens et al. (1988) Stefański and Kowalczyk (1991) Sinnemann et al. (1990)	 (19) Stefański et al. (1994) (20) Lin et al. (1991) (21) Solzi et al. (1990) (22) Okada et al. (1990) (23) Moze et al. (1991) 	

Table 14, continued

210 т_с [К] 800 700 600 Y(Fe1_xCox)10Si2 500 0.2 0.4 0.6 0.8 1.0 0

Fig. 23. Curie points versus Co concentration x in $Y(Fe_{1-x}Co_x)_{10}Si_2$ alloys (Buschow 1988a, Q. Li et al. 1991).

(Q. Li et al. 1991), which corresponds to the magnetic moment of the iron sublattice. This value is higher than for any other silicide, suggesting antiferromagnetic coupling between the Fe and R (heavy) sublattices. The magnetic moment for the rare-earth sublattice equals 6.4, 8.0, 8.6, 8.3 and 7.5 $\mu_{\rm B}/{\rm R}$ atom for Gd, Tb, Dy, Ho, and Er, respectively. These values are different from the free-ion values, and the discrepancy most probably results from a contribution of the conduction electrons to magnetism. The compounds of Ni exhibit weak magnetic properties (Moze et al. 1992). This seems to result not only from geometric factors (distribution of the atoms in the crystallographic positions) but predominantly from a band structure with a filled 3d Ni band.

As mentioned above, no RCo₁₀Si₂ compound has been reported, but SmFe_{10-x}Co_xSi₂ (Buschow et al. 1988, Solzi et al. 1990) and YFe_{10-x}Co_xSi₂ (Buschow 1988a) are formed over a limited composition range. Figure 23 shows that, for the Y silicides, as the Co concentration x increases, $T_{\rm C}$ increases from 569 K for x=0 (Q. Li et al. 1991) to above 800 K (Buschow 1988a) with further diminution of $T_{\rm C}$ up to the solubility limit (x = 8).

Buschow et al. (1988) and Solzi et al. (1990) have reported the existence of Sm pseudoternaries up to x = 5 with an increase of $T_{\rm C}$ from 606 K (Buschow 1988a) to above 800 K (Solzi et al. 1990). The temperature dependences of anisotropy and critical field for the first-order magnetization process (FOMP) both exhibit a flattening with increasing Co content. Unfortunately, the alloys investigated by Solzi et al. (1990) are reported to exhibit about 20% of second phases: α -Fe–Co(–Si) alloy, Sm₂Fe_{17-x}Co_x, and free cobalt.

3.3.1.2. Compounds with Ti. The lattice parameters and magnetic data for compounds with Ti are listed in tables 15a-d. Their stoichiometry only exceptionally corresponds to the $RM_{10}Ti_2$ formula and the index for Ti is usually <2. The compounds are formed with Fe, Co, and solid solutions in which Fe is substituted by Co or Ni. As mentioned above, the compounds with Ti and V seem to be the most promising magnetic materials.

						Ternary	RFe _{12-x} Ti _x .	type compounds		
R	x	a	v	$T_{ m c}$	$M_{\rm s}^{\rm M}$	H_{a}	$H_{ m hf}$	Remarks	Ref.	ت
		(uu)	(uu)	(K)	$(\mu_{\rm B}/{ m fu})$	(I)	E			1
×	1.2	0.8509	0.4789	520				easy axis	1	
	1.2				19.12 ^d	5.0 ^d			5	
	1.1	0.8525	0.4800	510	17.69 ^a	3.47°			с , с	
				(0)105	14.89°	2.17	3(1)0 71	STEAME atom distribution CEE nonmators	r 4	
	1.0	0.851(2)	0.478(3)	(6)475	19.0(2)° 18.92°	4.0(3) ^d 2.0(3) ^d	2(6)0.07	- re MLS, atom distribution, CEr parameters	14	
					16.2 ^d				4	
	1.0	0.8503	0.4800				23.52 ^d	⁵⁷ Fe ME, Fe atom distribution	5	
	1.0	0.85093	0.47974	518	16.48°				y y	
					16.15				0	
	1.0	0.85093(2)) 0.47974(2)				27.6°	ND, atomic parameters ⁵⁷ Fe ME	8	
							24.1 ^d		8	
Ce	1.0	0.853	0.478	~450	1.55 ^{b,e} 1.10de	7.0 ^b			9.9	
ć		0.960	0.470	~500	1.19 te	- 6.2			× 0	
Ľ	1.0	0.000	614.0		1.38 de				6	
PN	1.1	0.8577	0.4819	547		1.0 ^d			3	
	1.0	0.856	0.478	547	16.8 ^d		27.7 ^d	⁵⁷ Fe ME, Fe atom distribution, CEF parameters	4 4	
	Ċ	0 0551	1787	551	1.77 ¹ 13 0d	2 6d			4	
	7.0	10000		100	1.01	2		photoemission and spin polarized calculation	Π	
λPN	2							$T_{\rm sk}$ vs. Nd concentration	12	
Sm	1.2	0.8561	0.4792	585				1	13	
	1.0	0.856	0.479						14	
	1.0	0.856	0.479			12.7°		S.C.	15	
						8.3 ^d			15	
	1.1	0.8576	0.4800	585	14.08 ^a	10.2°		$H_{\rm cr}({\rm FOMP}) = 8.22 \ {\rm T}^{\circ}$	3	
					17.24 ^d	9.22 ^d			3	
									continued on next page	9)

Table 15a RFe_{12-x} Ti_x-type compounds

R	×	а	c	$T_{\rm C}$	$M_{\rm s}^{\rm M}$	H_{a}	$H_{ m hf}$	Remarks	Ref.
		(uu)	(uu)	(K)	$(\mu_{\rm B}/{ m fu})$	(E)	(T)		
Sm (ct ù)	1.0	0.854	0.478	584	17.1 ^d 1.8 ^f	10.5 ^d	28.3°	⁵⁷ Fe ME, Fe atom distribution, CEF parameters	4 4
	1.0 1.0				20.46 ^b 18.15 ^d			$T_{SR} = 150 \text{ K}$, $H_{cr}(\text{FOMP}) = 9 \text{ T}$, $H \parallel c$ CEF analysis, high field magnetization	16 17 17
	1.0	0.8558	0.4793	597	20.77℃ 18.41 ^d	22.1 ° 8.3 d		s.c., atomic positions	18
	1.0						28.7° 25.8 ^d	⁵⁷ Fe ME, thin film	~~~~~
Sm*	2/1	0.8575	0.4800	610	15.6 ^a	26.81 ^ª		SmFe ₁₀ Ti, $K_1(4.2K) = 12.1 \times 10^7 \text{ erg/cm}^3$, and $K_1(293 \text{ K}) = 1.5 \times 10^7 \text{ erg/cm}^3$. 19
		0.850	0.479		14.1	- 64-01		Magneto-optical studies of perpendicularly textured sputtered films	20
Gd	1.2	0.8522	0.4783	600				easy axis	1,21
	1.2				13.36 ^b	7.0 ^b			6
	1.1	0.8547	0.4806	601	12.06 ^ª 12.06 ^d	5.11° 3.63 ^d			ო ო
·	1.0	0.850	0.477	607	1.81 ^{b,f} 12.5 ^d		28.2 °	37 Fe ME, Fe atom distribution, CEF parameters	4 4
	1.0	0.8530	0.4784	522	11.8° 11.9°	7.81 ° 5.85 d		axial anisotropy at RT	22
-	1.0	0.8548	0.4800	610	12.46 ^a 11.81 ^d				23 23
	1.0						25.06 ^d	⁵⁷ Fe ME, Fe atom distribution	Ś
	17	0.8523	0.4783	600			17.5 ^d 28.1℃	⁵⁷ Fe ME, CEF parameter, $A_2^0 = -79 \text{ K}/a_0^2$ ⁵⁷ Fe ME	24 8
							25.3 ^d		œ
								continued on nex	t page

Table 15a, continued

W. SUSKI

						-	Table 15a,	continued	
~	×	a (nm)	(um)	(K)	$M_{\rm s}^{\rm M}$ ($\mu_{\rm B}/{ m fu}$)	H _a (T)	H _{hf} (T)	Remarks	Ref.
Tb	1.0	0.8534	0.4802	459	10.2ª			$T_{\rm SR} = 200$ K, easy plane anisotropy	6.4
	1.0	0.851	0.477	554	9.7 ^b 10.6 ^d		28.6°	³⁷ Fe ME, Fe atom distribution, CEF parameters	444
	1.0	0.8537	0.4808	580	9.18 ² 9.18 ² 10.85 ^d				53 3
	1.0			560 ₽	11.0 ^b			s.c., $<3\%$ α -Fe, $T_{\rm SR}$ (basal plane) uniaxial, sensitive to magn. field	25
Dy	1.1	0.8520	0.4800	534	8.54ª 10 54ª	2.75 ^d		$T_{sk1} = 90 \text{ K}$, $T_{sk2} = 185 \text{ K}$, cone at LN ₂	с , с
	1.0	0.848	0.477	534	9.7 ^b 11.3 ^d	2.3 ^d	28.9°	⁵⁷ Fe ME, Fe atom distribution, CEF parameters	44
	1.0	0.8510	0.4790	522	1.85 ^f 10.7 ^c 11.6 ^d	4.32 ^d		axial anisotropy at RT	4 26 26
	1.0	0.8521	0.4799	560	9.80 ^a				3 23 2
	1.0							s.c. magnetic moment: $ (100) $ at $T < 58$ K; canted spin structure at $58 \rightarrow 200$ K; $ c-axis$ at $T > 200$ K; three FOMP under fields below	27
				550 609(1)			52 ^b	1.0 K, CEF parameters s.c. $T_{SR1} = 120$ K (axis-cone), $T_{SR2} = 220$ K ¹⁶¹ Dy ME SRT at 17 $T_{c} = 120$ K (come anole 80°): $120 \le T \le 220$ K (T_{c}) (com	28 29
								angle 45°); above T_{sg2} – axial s.c. $T_{\text{sg1}}(\chi_{ac}) = 69 \text{ K}$, $T_{\text{sg2}}(\chi_{ac}) = 187 \text{ K}$, under $H > 0.2 \text{ T}$ T_{sg1} becomes I order	30

213

continued on next page

							Table 15a,	continued	
~	×	a (nm)	<i>c</i> (nm)	T _c (K)	$M_{ m s}^{ m M}$ $(\mu_{ m B}/{ m fu})$	H _a (T)	Н _ы (Т)	Remarks	Ref.
Но	1.1	0.8505	0.4793	510	9.58 ^b 12.22 ^d	2.50° 2.83 ^d		$H_{\rm cr}({\rm FOMP}) = 1.89 \text{ T}$ at LN ₂	6.6
	1.0 1.0	0.847 0.8479	0.477 0.4779	520 505	1.75 ^f 10.2 ^c 12.4 ^d	4.57 ^d	27.3°	⁵⁷ Fe ME, Fe atom distribution, CEF parameters axial anisotropy at RT	26 26
	1.0	0.8506	0.4799	544	9.58 ^ª 12.15 ^d				23 23
Er	1.1	0.8525	0.4802	500	10.38 ^a 13.25 ^d	5.84° 2.63 ^d		$H_{\rm cr}({ m FOMP}), T_{ m SR} pprox 80 { m K}$	ო ო
	1.0	0.846	0.477	505	9.2 ^b 12.4 ^d 1.71 ^f	8.3 ^b 3.6 ^d	26.7°	⁵⁷ Fe ME, Fe atom distribution, CEF parameters	444
	1.0	0.8477	0.4780	495	11.0 ^b 13.4 ^d	8.97° 4.59 ^d		axial anisotropy at RT	22
	1.0	0.8495	0.4795	530	9.90 ^ª 12.54 ^d				23 23
	1.0	0.84705	0.47792	504	9.64ª 12.04 ^d				99
								$K_1(T), T_{\max} \approx 110 \mathrm{K}$ $T_{\mathrm{SR}} \approx 50 \mathrm{K}$	31 32
Lu	1.0	0.846 0.846	0.477 0.477	496	1.75' 1.65 ^f 15.7 ^d	2.2 ^d	27.4° 25.7°	⁵⁷ Fe ME, Fe atom distribution, CEF parameters ⁵⁷ Fe ME, Fe atom distribution, CEF parameters ⁵⁷ Fe ME, Fe atom distribution, CEF parameters s.c., $K_1(T)$	4 4 4 6 31

214

continued on next page

	lable 13a, notes	
 Variable composition; see Remarks column. 	° At 77 K.	f ln $\mu_{\rm B}/{\rm Fe}$ atom.
^a At 1.5 K.	^d At 293 K.	^g <i>c</i> -axis.
^b At 4.2 K.	° In Tesla.	
References		
(1) Buschow et al. (1988)	(12) Luong et al. (1990)	(23) Cao et al. (1992)
(2) Verhoef et al. (1988)	(13) Buschow (1988a)	(24) Dirken et al. (1989)
(3) J. Hu et al. (1988)	(14) Ohashi et al. (1987)	(25) Andreev et al. (1993a)
(4) BP. Hu et al. (1989a)	(15) Ohashi et al. (1988b)	(26) Sinha et al. (1989a)
(5) Ge et al. (1992)	(16) HS. Li et al. (1988)	(27) BP. Hu et al. (1990)
(6) Solzi et al. (1988)	(17) Kaneko et al. (1989)	(28) Andreev et al. (1990)
(7) Moze et al. (1988b)	(18) Ohashi et al. (1988a)	(29) Gubbens et al. (1991)
(8) Sinnemann et al. (1989b)	(19) Yang et al. (1988a)	(30) Garcia et al. (1993)
(9) Akayama et al. (1994)	(20) Cadieu et al. (1993)	(31) Andreev et al. (1988)
(10) Chin et al. (1989)	(21) de Mooij and Buschow (1988)	(32) Sinha et al. (1989b)
(11) Fernando et al. (1993)	(22) Christides et al. (1989)	

te 15.9 Table

R	а	с	$T_{\rm C}$	M_{s}^{M}	Remarks	Ref
	(nm)	(nm)	(K)	$(\mu_{\rm B}/{ m fu})$		
Y			1050	10.62°	axial anisotropy at RT	1
	0.83479	0.47004	943	12.69 ^b		2
				12.93°		2
				13.70ª		3
La			980	12.63 °		1
Ce			920	13.10°	axial anisotropy at RT	1
Pr			1040	15.36°	axial anisotropy at RT	1
Nd			1020	15.27°	axial anisotropy at RT	1
Sm			1040	12.80°	planar anisotropy at RT	1
Gd			1055	7.56°	axial anisotropy at RT	1
	0.8394	0.4716	1080	7.8 ^b	axial anisotropy at RT	4
				9.3°		4
Tb			1070	7.2°	axial anisotropy at RT	1
Dy	0.8108	0.5491			axial anisotropy at RT	4
			1030	9.30°	axial anisotropy at RT	1
Но	0.8416	0.4653	1073	6.0 ^b	axial anisotropy at RT	4
				10.6°		4
			1045	12.11 °	axial anisotropy at RT	1
Er	O.8381	0.4724	1066	13.0 ^b	axial anisotropy at RT	4
				12.7°		4
			1060	11.44°	planar anisotropy at RT	1
^a At 1.5	5 K.		^b At 77 K.		^c At 293 K.	

Table 15b Ternary RCo₁₁Ti-type compounds

References

(1) Ohashi et al. (1991)

Some of the Co compounds demonstrate Curie points above 1000 K, however, higher magnetization values are observed for the Fe compounds. In both series, a comparison of the high value of the saturation magnetic moment for Y compounds with those observed for other rare earths proves that for light lanthanides the magnetic moments of both sublattices are coupled ferromagnetically, whereas for the heavy lanthanides they are antiferromagnetic. Therefore, much investigation has been directed at alloys in which Fe is substituted by Co in order to enhance $T_{\rm C}$ without excessive reduction of the magnetization. Figure 24 (J. Hu et al. 1988) shows the lattice parameters of the RFe_{10.9}Ti_{1.1} compounds. One can see the lanthanide contraction but also a pronounced increase of both lattice parameters for Er. Because a change of valence seems to be excluded for this element, this anomaly should have an other reason. The temperature dependence of magnetization of Sm and Ho alloys shows a small decrease for Sm and a small increase for Ho with

⁽²⁾ Solzi et al. (1988)

⁽³⁾ Yang et al. (1990)(4) Sinha et al. (1989a)

a c T_{c} M_{u}^{v} H_{u} Remarks Ref. (mm) (m) (K) (μ_{u}/μ) (T) (T) T 1 $f(v)$						Ternary RFe	Table I. 11-yCoyTix	5c -type con	sponods	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	×	1	a (nm)	c (nm)	T _c (K)	$M_{\rm s}^{\rm M}$ ($\mu_{\rm B}/{ m fu}$)	H _a (T)	H _{hf} (T)	Remarks	Ref.
I (30) $f(y)$	1.0	1	f(y)	f(y)	f(y)	$f(y)^a$				
	1.0		, ,			1.3(2) ^b		f(y)	⁵⁷ Fe ME, Fe atom distribution, minimum in H_{hf} vs. y at $y = 0.6$; $H_{hf} = 27.7$ T	5
							f(y)			ŝ
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1.0								⁵⁷ Fe ME	4
			f(y)	f(y)						Ś
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1.0		f(y)	f(y)	f(y)	f(y)	$f(y)^{\mathfrak{c},\mathfrak{d}}$			9
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1.0		f(y)	f(y)	f(y)					٦
$H_c = 0.5 \rightarrow 0.6$ T, $(BH)_{max} = 90.4$ kJ m ³ (11.3 MG0e)80.85500.479261518.33'8.46°s.c., $(BH)_{max} = 2.80$ MG0e90.85510.478572019.28°8.21°s.c., $(BH)_{max} = 3.16$ MG0e90.85510.478582018.61°7.10° $(BH)_{max} = 2.90$ MG0e90.85530.476887020.45°4.80° $(BH)_{max} = 3.58$ MG0e90.85380.476796019.71°9.80° $(BH)_{max} = 3.53$ MG0e90.84980.476796019.71°9.80° $(BH)_{max} = 3.53$ MG0e90.825120.477283413.3^d7.69^daxial anisotropy at RT110.85120.477293413.3.67.69^daxial anisotropy at RT110.84710.475299513.6^dplanar anisotropy at RT110.84710.477211910.9^dplanar anisotropy at RT1111.6°13.9°planar anisotropy at RT111111.6°11.910.9^dplanar anisotropy at RT11	1.2						f(y)			£
0.8560 0.4792 615 18.33° 8.46° s.c., $(BH)_{max} = 2.80 \text{MGOe}$ 9 0.8351 0.4785 720 19.28° 8.21° s.c., $(BH)_{max} = 3.16 \text{MGOe}$ 9 0.8351 0.4785 820 18.61° 7.10° $(BH)_{max} = 3.16 \text{MGOe}$ 9 0.8353 0.4785 820 18.61° 7.10° $(BH)_{max} = 3.58 \text{MGOe}$ 9 0.8353 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.58 \text{MGOe}$ 9 0.8498 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.53 \text{MGOe}$ 9 0.8498 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.53 \text{MGOe}$ 9 0.8491 0.4772 834 13.3 ^d 7.69 ^d axial anisotropy at RT 11 0.8471 0.4772 995 13.6 ^d axial anisotropy at RT 11 11 13.9 ^d 7.69 ^d axial anisotropy at RT 11 0.8471 0.4772 995 13.6 ^d planar anisotropy at RT 11 0.8419 0.4727 110 <	1.0								$H_{\rm C} = 0.5 \rightarrow 0.6 \text{ T}, (BH)_{\rm max} = 90.4 \text{ kJ m}^3 (11.3 \text{ MGOe})$	8
0.8551 0.4785 720 19.28° 8.21° $s.c.$, $(BH)_{max} = 3.16 MGOe$ 9 0.8351 0.4785 820 18.61° 7.10° $(BH)_{max} = 2.96 MGOe$ 9 0.8353 0.4763 870 20.45° 4.80° $(BH)_{max} = 2.96 MGOe$ 9 0.8353 0.4763 870 20.45° 4.80° $(BH)_{max} = 3.53 MGOe$ 9 0.8498 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.53 MGOe$ 9 0.8491 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.53 MGOe$ 9 0.84512 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.53 MGOe$ 9 0.8451 0.4772 834 13.3^{d} 7.69^{d} axial anisotropy at RT 11 0.8471 0.4772 935 13.6^{d} 7.69^{d} axial anisotropy at RT 11 0.8419 0.4727 119 10.9^{d} 10.841 10.9^{d} 11.6^{d} 0.8419 0.4727 119^{d} <td>1.0</td> <td></td> <td>0.8560</td> <td>0.4792</td> <td>615</td> <td>18.33°</td> <td>8.46[°]</td> <td></td> <td>s.c., $(BH)_{\text{max}} = 2.80 \text{ MGOe}$</td> <td>6</td>	1.0		0.8560	0.4792	615	18.33°	8.46 [°]		s.c., $(BH)_{\text{max}} = 2.80 \text{ MGOe}$	6
0.8551 0.4785 820 18.61° 7.10° $(BH)_{max} = 2.96 M G O e$ 9 0.8538 0.4768 870 20.45° 4.80° $(BH)_{max} = 3.58 M G O e$ 9 0.8438 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.58 M G O e$ 9 0 8498 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.53 M G O e$ 9 0 8498 0.4767 960 19.71° 9.80° $(BH)_{max} = 3.53 M G O e$ 9 0.8512 0.4772 834 13.3° 7.69° $axial anisotropy at RT$ 11 0.8512 0.4772 834 13.3° 7.69° $axial anisotropy at RT$ 11 0.8471 0.4752 995 13.6° 5.38° $planar anisotropy at RT$ 11 0.8419 0.4727 1109° $planar anisotropy at RT$ 11 11.6^{\circ} 11.6° $planar anisotropy at RT$ $planar anisotropy at RT$ $planar anisotropy at RT$ $planar anisotropy at RT$	1.0		0.8551	0.4785	720	19.28°	8.21 °		s.c., $(BH)_{max} = 3.16 MGOe$	6
0.8538 0.4768 870 20.45^c 4.80^c $(BH)_{max} = 3.58 MGOe$ 9 0 8498 0.4767 960 19.71^c 9.80^c $(BH)_{max} = 3.53 MGOe$ 9 0 8498 0.4767 960 19.71^c 9.80^c $(BH)_{max} = 3.53 MGOe$ 9 0 8312 0.4772 834 13.3^d 7.69^d axial anisotropy at RT 11 0.8512 0.4772 834 13.3^d 7.69^d axial anisotropy at RT 11 0.8471 0.4752 995 13.6^d planat anisotropy at RT 11 0.8419 0.4727 1119 10.9^d planat anisotropy at RT 11 11.6^c 10.9^d 10.9^d 11.6^c 11.6^c 11.6^c 11.6^c 11.6^c 11.6^c	1.0		0.8551	0.4785	820	18.61 °	7.10℃		$(BH)_{\text{max}} = 2.96 \text{ MGOe}$	6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1.0		0.8538	0.4768	870	20.45°	4.80°		$(BH)_{\text{max}} = 3.58 \text{ MGOe}$	6
0.8512 0.4772 834 13.3 ^d 7.69 ^d axial anisotropy at RT 11 0.8512 0.4772 834 13.3 ^d 7.69 ^d axial anisotropy at RT 11 14.0 ^e 5.38 ^e axial anisotropy at RT 11 11 0.8471 0.4752 995 13.6 ^d 11 11 13.9 ^e 13.9 ^e planar anisotropy at RT 11 11 0.8419 0.4727 1119 10.9 ^d 11 11.6 ^e 11.9 ^e planar anisotropy at RT 11	1.0	_	0 8498	0.4767	960	19.71°	9.80°		$(BH)_{\text{max}} = 3.53 \text{ MGOe}$	6
0.8512 0.4772 834 13.3 ^d 7.69 ^d axial anisotropy at RT 11 14.0 ^e 5.38 ^e 95 13.6 ^d 11 11 0.8471 0.4752 995 13.6 ^d 13 11 0.8471 0.4752 995 13.6 ^d 11 11 0.8419 0.4727 1119 10.9 ^d 11 11.6 ^e 11.6 ^e 11.6 ^e 11.6 ^e 11									⁵⁷ Fe ME, Fe atom distribution	10
14.0° 5.38° 11 0.8471 0.4752 995 13.6 ^d 11 13.9° 13.9° 11 11 0.8419 0.4727 1119 10.9 ^d 11 11.6° 11.6° 11.6° 11	Ι		0.8512	0.4772	834	13.3 ^d	2.69 ^d		axial anisotropy at RT	11
0.8471 0.4752 995 13.6 ^d planar anisotropy at RT 11 13.9 ^c 13.9 ^c 13.9 ^c 11 11						14.0°	5.38°			11
13.9° 11.9° 10.9° 11 0.8419 0.4727 1119 10.9° 11 11 11.6° 11 11.6° 11			0.8471	0.4752	995	13.6 ^d			planar anisotropy at RT	11
0.8419 0.4727 1119 10.9 ^d planar anisotropy at RT 11.6 ^c 11						13.9°				11
11.6° 11	1		0.8419	0.4727	1119	10.9 ^d			planar anisotropy at RT	11
						11.6°				11

						Ta	ble 15c, <i>co</i>	ntinued		
ж	ý	×	a (mn)	<i>с</i> (пт)	<i>T</i> _c (K)	$M_{\rm s}^{\rm M}$ $(\mu_{\rm B}/{ m fu})$	H _a (T)	H _h (T)	Remarks	Ref.
Dy	-	-	0.8520	0.4779	636	11.4 ^d 13.1°	4.42°		axial anisotropy at RT	= :
	ς.	1	0.8492	0.4765	820	11.7 ^d 13.9°	4.72°		axial anisotropy at RT	1 1 1
	9	1	0.8447	0.4742	1022	10.2 ^d 13.0 ^c			axial anisotropy at RT	= = :
	6	1	0.8393	0.4714	1095	8.0 ^d 10.5 ^c			axial anisotropy at RT	= = =
Но	0,1,3 3	1	0.8469	0.4761	810	12.1 ^d 15.1 ^c	4.8°		$T_{\text{SRI}} = 50 \text{ K}$, $T_{\text{SR2}} = 250 \text{ K}$; planar for $T < T_{\text{SRI}}$; cone for $T_{\text{SRI}} < T < T_{\text{SR2}}$; axial for $T > T_{\text{SR2}}$ axial anisotropy at RT	
	3								$T_{\text{SR1}} = 50 \text{ K}$, $T_{\text{SR2}} = 250 \text{ K}$; cone for $T_{\text{SR1}} < T < T_{\text{SR2}}$; axial for $T > T_{\text{SR2}}$	12
^a At 1.5 ^b In μ _B	5 K. 'Co atom.							• At 293] 4 At 77 K	×	
<i>Referen</i> (1) Yang (2) Z.W. (3) Solzi (4) J. Hu	<i>ces</i> et al. (198 Li et al. (1 et al. (199 et al. (199	8b) 991a) 0)			 (5) Ohas (6) Chen (7) Q. Li (8) Ding 	hi et al. (1988 g et al. (1988 et al. (1991) and Rosenbe	8b) ;) rg (1990a)		 (9) Zolotukhin et al. (1993) (10) Zeng et al. (1991) (11) Sinha et al. (1989a) (12) Sinha et al. (1989b) 	

					Table	e 15d			
				Ternary	miscellaneou	noduoo st	nds with	Тi	
Compound	×	a (mm)	c (nm)	T _c (K)	$M_{\rm s}^{\rm M}$ ($\mu_{\rm B}/{ m fu}$)	Ha (T)	H_{hf} (T)	Remarks	Ref
(Er _{0.5} Sm _{0.5})Fe _{11-x} Co _x Ti	0	0.8507	0.4784	533	14.5 ^ª 14.8 ^b	15.18 ^a 9.00 ^b		axial anisotropy at RT	1
$(Er_{0.5}Sm_{0.5})Fe_{11-x}Co_{x}Ti$	3.0	0.8507	0.4769	823	16.3 ^ª 17.9 ^b	9.00 ^a 4.05 ^b		axial anisotropy at RT	1 1
Y(Fe _{1-x} Ni _x) ₁₁ Ti	$0 \leqslant x \leqslant 0.3$			$f(\mathbf{x})$	$f(\mathbf{x},H)^{\mathfrak{c}}$			anisotropy constants	7
$Y(Fe_{1-x}Ni_{y})_{11}Ti$	$0 \leqslant x \leqslant 0.6$			$f(\mathbf{x})$	f(x) 0.6 ^d		$\int (x) f(x)$	⁵⁷ Fe ME, hyperfine parameters, atomic distribution ⁵⁷ Fe ME, maximum in H_{hf} vs. x at $x = 0.21$, $H_{hf} \max = 24.1$ T	ω4
$Y(Fe_{1-x}Si_x)_{11}Ti$	$0 \leqslant x \leqslant 0.1$			f(x)	$f(x,H)^{\mathfrak{c}}$			anisotropy constants	7
^a At 77 K. ^b At 293 K.						° At 1. ^d In μ _B	5 K. /Ni aton	T	
References (1) Sinha et al. (1989a) (2) Yang et al. (1988b)						(3) Z.V (4) Oh	V. Li et a ashi et a	.l. (1990) l. (1988a)	

.



Fig. 24. Lattice parameters a (lower panel) and c (upper panel) for RTi_{1.1}Fe_{10.9} alloys (J. Hu et al. 1988).

increasing temperature, as shown in fig. 25 (J. Hu et al. 1988). In turn, the same plot for the Dy compound exhibits an anomaly at a temperature corresponding to the spin-reorientation transition (SRT). The anomaly seen in the temperature dependence of the hyperfine field $H_{\rm hf}$ for the Nd, Tb and Dy compounds of the RFe₁₁Ti-type (fig. 26) is



Fig. 25. Magnetization, M, versus temperature measured under magnetic field of 6 T for SmTi_{1.1}Fe_{10.9} (upper curve) and HoTi_{1.1}Fe_{10.9} (lower curve) compounds. Inset shows M(T) plot for DyTi_{1.1}Fe_{10.9} measured under magnetic field of 0.2 T (J. Hu et al. 1988).



Fig. 26. Hyperfine fields, $H_{\rm hf}$ at different crystallographic sites for (a) R=Nd, (b) R=Tb and (c) R=Dy versus temperature in RFe₁₁Ti alloys, obtained by ⁵⁷Fe ME experiments. The discontinuity corresponds to the spin-reorientation temperature, $T_{\rm SR}$ (B.-P. Hu et al. 1989b).

also due to a SRT (B.-P. Hu et al. 1989b). Admixture of Co for Fe is possible only over a limited range $x \leq 3$ in RFe_{11-x}Co_xTi alloys, except in those containing Gd and Dy (Sinha et al. 1989a), and Sm, where the limit is $x \leq 5$ (Andreev et al. 1989). Figure 27 presents



Fig. 27. (Upper panel) Lattice parameters a and c, (middle panel) Curie points $T_{\rm C}$, and (lower panel) saturation induction, M_s versus Co concentration x in Sm(Fe_{11-x}Co_x)Ti alloys (Andreev et al. 1989). Note that, contrary to results of Ohashi et al. (1988b) the single-phase range exists for x < 5 only. The Curie points obtained by Ohashi et al. (1988b) are slightly higher than that presented in this figure, except for x=0, where the value shown in the figure is apparently higher. Results of Solzi et al. (1990) (diamonds) are also similar.

W. SUSKI

some parameters for the Sm pseudoternaries which are presented according to Andreev et al. (1989). As mentioned, the alloys exist over a limited composition range in which increasing x corresponds to increasing T_c , whereas the saturation magnetization exhibits a maximum at x = 3. The same trends are reported for the compounds of Gd and Dy (Sinha et al. 1989a). An admixture of Ni is reported to be possible also over a limited range of composition in YFe_{11-x}Ni_xTi (Yang et al. 1988b, Z.W. Li et al. 1990, 1991). In these alloys the magnetic moment of Ni is determined to be constant, whereas the moment of Fe exhibits a maximum for $1 \le x \le 3$ (Z.W. Li et al. 1991). The Curie points in turn have been reported to increase up to about 600 K for x = 3 (Yang et al. 1988b).

Finally, one can see from table 15a that alloys of the $YFe_{11-x}Si_xTi$ -type were also investigated (Yang et al. 1988b). However, the substitution of Si instead of Fe decreases T_C as well as the anisotropy constants.

3.3.1.3. Compounds with V. Magnetic properties of compounds with V are presented in table 16, which besides the Ti compounds lists some other of the most frequently investigated materials. The range of existence of $RM_{12-x}V_x$ alloys extends mostly for $1.5 \le x \le 4.0$, however, a higher limit is observed for Y, Tb and Er. The most popular index is x = 1.5-2.0. Figure 28 presents the lattice parameters for $RFe_{10.9}Ti_{1.1}$ systems (fig. 24) both lattice parameters demonstrate the regular lanthanide contraction. The Curie points do not exceed 600 K for compounds with Fe, and among the Co compounds only $DyCo_{10}V_2$ shows a much higher $T_C = 840$ K (Jurczyk et al. 1991a). A still higher T_C was observed for $DyFe_2Co_8V_2$, however, the saturation magnetization for this composition is low (Jurczyk et al. 1991b). Inspection of the saturation magnetization for individual



Fig. 28. Lattice parameters a (left-hand scale) and c (right-hand scale) for RFe₁₀V₂ compounds (de Mooij and Buschow 1987).

					Tern	ary R(Fe, t	$Co)_{12-x}V_x$ -	type compounds	
~	*	a (uu)	رسا) د	I _c	$M_{\rm s}^{\rm M}$ ($u_{\rm s}/f_{\rm H}$)	H_{a}	H _{li}	Remarks	Ref.
Ternar	y RFe ₁₂	-*Vx compou	uds						
Y	2.0	I			16.15*				1
	2.0					2.2 ^b		Stevens operators = 0	2
	2.0	0.8501	0.4775	540				easy axis for Fe sublattice, $A_2^0 = -140 \text{ K}/a_0^2$	3,4
	2.0	0.84903(3)	0.47725(2)		17.13ª			easy axis, ND: atomic parameters, V in 8(i)	5
	2.0				16.15 ^a	~5.0ª			6
	1.6				17.93 ª	5.0			9
	2.6				13.11ª				9
	3.5				9.64ª				9
	2.0	0.84739	0.47617	528	15.30°			atomic positions	7
					14.24 ^d				7
	1.5	0.84727	0.47699	575	16.03 °				7
					14.91 ^b				7
	1.5			575		2.53 ^b			8
	2.0			528		1.90^{b}			8
	2.75			439		0.7 ^b			8
	4.0			373					8
	2.0						23.2°	⁵⁷ Fe ME	6
	2.0							⁵⁷ Fe ME, site occupation	10
	2.0						23.3ª	⁵⁷ Fe ME	11
							23.2°	⁵⁷ Fe ME	11
							20.2 ^b	⁵⁷ Fe ME	11
	2.0						22.7 ^d	⁵⁷ Fe ME	12
	1.5						25.5 ^d	^{s7} Fe ME	12
	2.8						18.6 ^d	⁵⁷ Fe ME	12
	4.0						12.2 ^d	⁵⁷ Fe ME	12
	2.0						16.5 ^b	⁵⁷ Fe ME	13
පී	2.0						22.1℃	⁵⁷ Fe ME	12
								Ũ	ontinued on next page

Table 16 e, Co)_{12-x}V_x-type compc

ThMn-TYPE COMPOUNDS OF RARE EARTHS AND ACTINIDES

Ref.	1 2 15 1 15	15 15 15 15 15 15 15 15 15 15 15 15 15 1	20 20 23 23 23 24 11 23 25	26 26 27 27 28 next page
Remarks	CEF parameters ⁵⁷ Fe ME	The ME The M	ND, T_{SR} = 120 K, $\mu_{\text{te}} \ \mu_{\text{te}} \ $ at RT, at an angle at LT (4.2 K) ND, $T_{\text{SR}} = 120$ K, $\mu_{\text{te}} \ \mu_{\text{te}} \ $ at RT, at an angle at LT (4.2 K) χ_{ac} under pressure of 3.5 and 7.5 kbar and SRT CEF parameters atomic parameters atomic parameters ND, no SRT, atomic parameters $^{7}_{7}_{7}_{7}_{7}_{7}$ ME $^{7}_{7}_{7}_{7}_{7}$ ME $^{7}_{7}_{7}_{7}_{7}$ ME	S_{1}^{7} Fe ME S_{1}^{7} Fe ME S_{1}^{7} Fe ME SmFe ₁₀ TiV; at 10 K: $K_{1} = 6.1$, $K_{2} = 5.2$; at 300 K: $K_{1} = 1.4$, $K_{2} = 0.5 \times 10^{-7}$ erg/cm ³ ribbon, $H_{c} = 0.55$ T continued on
H ^R (E)	f(T)	f(T) f(T)	24.4° 22.6 ^b 25.2°	28.5° 24.9 ^b
H _a (T)	1.8 ^b		10.5 ^b ~5.4 ^b	
$M_{\rm s}^{\rm M}$ ($\mu_{\rm B}/{\rm fu}$)	18.07 ^a 12.9 ^b 20.7 ^a 18.2 ^b	18.4ª 18.4ª 17.2 ^b 15.7 ^b	11.55 ^b	7.23 ^b
7 _c (K)	570 583 630	605 580 570 594	610 591	
c (nm)	0.47772 0.4778 0.47	0.47 0.47 0.4768	0.47737(2) 0.47722 0.4776	0.4826
a (mn)	0.85630 0.8552 0.85	0.85 0.85 0.855 0.8525	0.85553(3) 0.85368 0.8538	0.8573
×	2.0 2.0 1.8	2.0 2.0 2.0 2.0	2.0 2.0 2.0 2.0 2.0 1.5	1.5 2/1
R	PN		Sa	Sm*

Table 16, continued

	Ref.	1 3,4	29	6	6	6	6		7	30			16	17	œ	œ	œ	×	20	1	7	21	16	16	18	17	20	31	32	ext page
uinued	Remarks	⁵⁷ Fe ME, easy axis of Fe sublattice, $A_2^0 = -140 \text{ K/}a_3^2$	⁵⁷ Fe ME, $A_2^0 = -144 \text{ K}/a_0^3$	⁵⁷ Fe ME	⁵⁷ Fe ME	⁵⁷ Fe ME	⁵⁷ Fe ME		CEF parameters	ND, crystallographic positions and atomic parameters; c is easy	axis at RT, 50.2° angle between easy axis and c at 4.2 K;	R-sublattice anisotropy prevails	$T_{\rm SR}^{\rm exp} = 170 {\rm K}, T_{\rm SR}^{\rm cule, {\rm CUF}} > 300 {\rm K}$	CEF parameters	$T_{\rm SR1} = 198 {\rm K}, \ T_{\rm SR2} = 2111 {\rm K}$				ND, $\mu_{\text{re}} \ \mu_{\text{Th}}$, c is easy axis at RT, tilt angle $f(T)$; SRT hystereti		CEF parameters	$\chi_{\rm ac}$ and SRT versus pressure up to 7.5 kbar	$T_{\rm sr} = 178$ K, $T_{\rm sr2} = 220$ K, axial anisotropy $T > RT$	$T_{\text{RPI}}^{\text{exp}} = 140 \text{ K}, T_{\text{RP2}}^{\text{exp}} = 215 \text{ K}, T_{\text{RP1}}^{\text{calls, CEF}} = 113,262 \text{ K}$	$T_{\rm SR} = 140$ K, below cone	$T_{sR} = 206 \text{ K}$, ⁵⁷ Fe ME, CEF parameters	$T_{sR} = 130 \rightarrow 150 \text{ K}$ (hysteresis), easy axis RT only	161 Dy ME, $T_{SR} = 190$ K	⁵⁷ Fe ME	continued on n
ole 16, con	$\stackrel{H_{\mathrm{hf}}}{(\mathrm{T})}$	11.4ª	11.45 ^a	25.9°	23.6ª	23.4°	18.8°																					702ª	22.5 ^c	
Tał	$_{a}^{H_{a}}$								3.2 ^b						1.27 ^b	3.32 ^b	4.50 ^b	4.02 ^b			3.9 ^b									
	$M_{\rm s}^{\rm M}$ ($\mu_{\rm B}/{ m fu}$)	8.93ª						7.92ª												4.52 ^ª										
	7 _c (K)	616 610	616					570					570		594	561	490	408		540			579	540		540				
	с (nm)	0.47741 0.4774	0.4778					0.47743		0.47713(1)									0.47662(2)	0.47733			0.4766				0.47658(3)		0.4773	
	a (mn)	0.85167 0.8517	0.8518					0.85023		0.84917(3)									0 84856(4)	0.84877			0 8484	2			0.84816(6)		0.8488	
	×	2.0	2.0	1.5	2.0			2.0		2.0			2.0	ì	1.5	2.0	2 L C	C - 7	0.0	2.0	ì	2.0	0 6	0.0	2.0	2.0	2.0	2.0		
	R	PD						đ												λΩ	ĥ									

	Ref.	- 0	ر 16	17 20	: = :	= =	1	30		33	7	7	7	16	34	œ	œ	17	œ	17	20	31	21			7	ct page
inued	Remarks		CEF parameters $T_{\text{exp}}^{\text{exp}} = 60 \text{ K}$, $T_{\text{sp}}^{\text{exc}}$ = 76 K	$T_{sR} = 60 \text{ K}$, CEF parameters <i>c</i> -asev axis at $4 2 \rightarrow \text{RT}$	STEME			ND, Fi, atomic parameters, p_0 at different positions, Er-sublattice	anisotropy parameters, at KT c-axis = easy axis, at 4.2 K easy axi. $\perp c$	$T_{SR} = 60 \text{ K}$ from axis to cone, CEF parameters			CEF parameters	$T_{\text{SR}}^{\text{exp}} = 65 \text{ K}$, $T_{\text{SR}}^{\text{cale},\text{CEF}} = 50 \text{ K}$	$T_{\rm SR} \approx 60$ K, below conical structure	$T_{ m SR} \approx 45 { m K}$	$T_{ m SR}pprox 60 m K$	$T_{\rm SR1} = 120 \rm K, \ T_{\rm SR2} = 139 \rm K$		$T_{\rm SR} = 65$ K, CEF parameters	ND, $T_{SR} = 50$ K, c-easy axis at RT, $\perp c$ at 4.2 K	166 Er ME	χ_{uc} and SRT under pressure of 3.5 and 7.5 kbar			CEF parameters	continued on ne
ole 16, cont	$_{\rm (T)}^{H_{\rm hf}}$				22.8ª	22.7° 19.0 ^b																$740(10)^{a}$					
Tal			2.24										1.5 ^b			2.67 ^b	1.69 ^b	0.39 ^b	0.91						-	1.7°	
	$M_{\rm s}^{\rm M}$ $(\mu_{\rm B}/{ m fu})$	6.35ª					8.37ª				8.31°	10.59 ^b												11.17ª	15.49ª		
	<i>T</i> _c (K)	525	525	525			505				508			505		546	508	435	348	505				496	483		
/	с (mn)	0.47672		0.47608(2)	(=)000120		0.47650	0.47644(2)			0.47562										0.47539(2) ^a			0.47608	0.47606		
	a a	0.84790		0 84661(4)	(+) TOOLO'O		0.84713	0.84627(3)			0.84507										$0.8451(4)^{a}$			0.84553	0.84468		
	×	2.0	2.0	00	2.0		2.0				2.0			2.0		1.5	2.0	2.75	4.0	2.0	2.0	2.0	2.0	2.0	2.0		
	м	Ho			Er																			Tm	Lu		

x a c T _c (m) m km km km rr (m) (m) (x) (μ_{a}/h) (T) (T) <th></th> <th></th> <th></th> <th></th> <th></th> <th>Tabl</th> <th>le 16, <i>con</i>i</th> <th>tinued</th> <th></th>						Tabl	le 16, <i>con</i> i	tinued	
rk Roh., V, compounds 35 24 0.8355 0.4698 185 35	×	a (nn)	(uu)	7c (K)	$M_{\rm s}^{\rm M}$ ($\mu_{\rm B}/{\rm fu}$)	H _a (T)	H _h (T)	Remarks	Ref.
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	ry RC	0 _{11-x} V, comp	spunoc						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2.4	0.8355	0.4698	185					35
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2.2	0.8347	0.4694	336					35
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2.0	0.8343	0.4692	428					35
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1.8	0.8348	0.4694	660					35
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.0				7.16 ^a				36
3.00.85090.4756686s.c., photoemission and spin polarization calculations385.00.84870.4741718Nd(Fe ₀₋₃ Co ₃)V ₂ : $T_{ss1} = 350$ K, planar anisotropy195.00.84870.4741718Nd(Fe ₀₋₃ Co ₃)V ₂ : $T_{ss1} = 350$ K, planar anisotropy195.00.84870.4741718Nd(Fe ₀₋₃ Co ₃)V ₂ : $T_{ss1} = 350$ K, planar anisotropy192.60.83740.4707207262.60.83740.4707207262.40.83700.4705277b27.7b2.20.83770.4697478262.30.833470.4697478262.00.833470.4691442262.00.833600.47108407(7)2.10.833600.47108407(7)2.20.833600.47108407(7)2.30.833600.47108407(7)2.00.833600.47108407(7)2.10.83280.4686427290, 615 K, axial anisotropy at RT2.00.83280.4686427294, 0.75, 758, vs. x		$f(\mathbf{x})$	f(x)	$f(\mathbf{x})$	$f(x)^{c,b}$	$f(x)^{c,b}$		$YFe_{10-r}Co_rV_2$	37
3.00.85090.4756686Nd(Fe _{10-x} Co _x)V ₂ : $T_{sx1} = 310$ K, planar anisotropy195.00.84870.4741718Nd(Fe _{10-x} Co _x)V ₂ : $T_{sx1} = 310$ K, planar anisotropy195.00.84870.4741718SimFe _{9,5} Co _x (V ₁₅ : $T_{sx1} = 350$ K, planar anisotropy192.60.83740.4707207262.60.83740.470720723.4 ^b 2.60.83740.470720723.4 ^b 2.60.83740.470720723.4 ^b 2.10.83620.4697478262.20.83620.46974782.00.83470.46974782.00.83470.46914422.00.83430.46914422.10.83060.47108407(x) $f(x)$ $f(x)$ $f(x)$ 2.10.83280.46664272.10.83280.46664272.20.83280.46664272.30.83280.46664272.00.83280.46664272.10.83280.46664272.10.83280.46664272.10.83280.46664272.10.83280.46664272.10.83280.46664272.10.83280.46664272.10.83280.46664272.10.83280.46664272.10.832		,						s.c., photoemission and spin polarization calculations	38
5.0 0.8487 0.4741 718 Nd(Fe _{10-C} Co _x)V ₂ : $T_{ss} = 350$ K, planar anisotropy 19 SimFe _{3,5} CoV _{1,5} : 5 Te ME 25 SimFe _{3,5} CoV _{1,5} : 5 Te ME 26 27.7 ^b SimFe _{3,5} CoV _{1,5} : 5 Te ME 26 27.7 ^b 27.7 ^b 27	3.0	0.8509	0.4756	686				Nd(Fe _{10-x} Co _x)V ₂ : $T_{SR1} = 310$ K, $T_{SR2} = 518$ K, planar anisotropy	19
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	5.0	0.8487	0.4741	718				$Nd(Fe_{10-x}Co_x)V_2$: $T_{SR} = 350 \text{ K}$, planar anisotropy	19
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$								SmFe _{9,5} CoV _{1,5}	25
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$							31.0°	SmFe _{9.5} CoV _{1.5} ; ⁵⁷ Fe ME	26
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$							27.7 ^b	- -	26
23.4 ^b 2.6 0.8374 0.4707 207 23.4 ^b 2.4 0.8370 0.4705 276 338 2.2 0.8362 0.4697 478 35 2.0 0.8347 0.4688 475 2.0 0.8343 0.4691 442 35 2.0 0.8360 0.4710 840 $f(T)$ $T_{SR1,2,3} = 10, 290, 615 K, axial anisotropy at RT 39 f(x) f(x) f(x) f(x) DyFe_{10-x}Co_x V_{2;} T_{SR} vs. x 14,392.0 0.8328 0.4686 427 35$							25.4°	$SmFe_{8,5}Co_2V_{1,5}$; ⁵⁷ Fe ME	26
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$							23.4 ^b		26
2.4 0.8370 0.4705 276 35 2.2 380 380 36 2.1 0.8362 0.4697 478 35 2.0 0.8347 0.4688 475 35 2.0 0.8343 0.4691 442 35 2.0 0.8343 0.4691 442 35 2.0 0.8360 0.4710 840 f(T) $T_{SR1,2,3} = 10, 290, 615 K, axial anisotropy at RT 39 2.0 0.8328 0.4686 427 20 015 K, axial anisotropy at RT 39 2.0 0.8328 0.4686 427 DyFe10-xCox V2; T_{2R} vs. x 14,39 $	2.6	0.8374	0.4707	207					35
2.2 380 35 2.0 0.8362 0.4697 478 35 2.0 0.8347 0.4688 475 35 2.0 0.8343 0.4691 442 35 2.0 0.8343 0.4691 442 35 2.0 0.8360 0.4710 840 $f(T)$ $T_{SR1,2,3} = 10, 290, 615 K, axial anisotropy at RT 39 2.0 0.8358 0.4686 427 39 32 2.0 0.8328 0.4686 427 39 $	2.4	0.8370	0.4705	276					35
2.0 0.8362 0.4697 478 35 2.0 0.8347 0.4688 475 35 2.0 0.8343 0.4691 442 35 2.0 0.8360 0.4710 840 $f(T)$ $T_{SR1,2,3} = 10, 290, 615 \text{ K}, axial anisotropy at RT 39 2.0 0.83560 0.4710 840 f(T) T_{SR1,2,3} = 10, 290, 615 \text{ K}, axial anisotropy at RT 39 2.0 0.8328 0.4686 427 DyFe10-xCoxV2; T_{SR} vs. x 14,39 $	2.2			380					35
2.0 0.8347 0.4688 475 35 2.0 0.8343 0.4691 442 35 2.0 0.8360 0.4710 840 $f(T)$ $T_{SR1,2,3} = 10, 290, 615 \text{ K}, axial anisotropy at RT 39 f(x) f(x) f(x) f(x) f(x) 14,39 2.0 0.8328 0.4686 427 39 2.0 0.8328 0.4686 427 39 $	2.0	0.8362	0.4697	478					35
2.0 0.8343 0.4691 442 35 2.0 0.8360 0.4710 840 $f(T)$ $T_{\text{SR1,2,3}} = 10, 290, 615 \text{ K}, \text{ axial anisotropy at RT}$ 39 2.0 0.8350 0.4710 840 $f(T)$ $T_{\text{SR1,2,3}} = 10, 290, 615 \text{ K}, \text{ axial anisotropy at RT}$ 39 2.0 0.8328 0.4686 427 14,39 2.0 0.8328 0.4686 427 35	2.0	0.8347	0.4688	475					35
2.0 0.8360 0.4710 840 $f(T)$ $T_{\text{SR1},2,3} = 10, 290, 615 \text{ K}$, axial anisotropy at RT 39 $f(x)$ $f(x)$ $f(x)$ $f(x)$ $f(x)$ DyFe _{10-x} Co _x $V_{2,i}$ T_{SR} vs. x 14,39 2.0 0.8328 0.4686 427 35	2.0	0.8343	0.4691	442					35
$f(x) \qquad f(x) \qquad f(x) \qquad f(x) \qquad f(x) \qquad DyFe_{10-x}Co_x V_2; T_{SR} \text{ vs. } x \qquad 14,39$ 2.0 0.8328 0.4686 427 35	2.0	0.8360	0.4710	840	f(T)			$T_{\text{SR}1,2,3} = 10, 290, 615 \text{ K}$, axial anisotropy at RT	39
2.0 0.8328 0.4686 427 35		$f(\mathbf{x})$	$f(\mathbf{x})$	$f(\mathbf{x})$	$f(\mathbf{x})$			$DyFe_{10-x}Co_x V_2$; T_{SR} vs. x	14,39
	2.0	0.8328	0.4686	427					35

227

continued on next page

 Variable composition; see Remarks column. At 4.2 K. At 2.2 K. At 2.3 K. At 293 K. At 293 K. Crössinger et al. (1987) Crössinger et al. (1992) Buschow et al. (1988) Buschow et al. (1988) Buschow et al. (1988) Helmholdt et al. (1988) Helmholdt et al. (1988) Verhoef et al. (1988) Simemann et al. (1988) Simnemann et al. (1989) Simnemann et al. (1989) Simnemann et al. (1989) Simnemann et al. (1989) Christides et al. (1990) Christides et al. (1990) Christides et al. (1990) Christides et al. (1991) Christides et al. (1991) Christides et al. (1991) 	Table 16, notes At 77 K. ^a At 10 K. ^a At 10 K. ^a At 10 K. (21) Arnold et al. (1993) (22) Buschow (1988a) (23) Ohashi et al. (1988a) (24) Simmemann et al. (1990) (25) Ding and Rosenberg (1990b) (25) Ding and Rosenberg (1990b) (26) Ding and Rosenberg (1990b) (27) Wang and Hadjipanayis (1990) (28) Okada et al. (1980) (29) Dirken et al. (1989) (30) Helmholdt et al. (1988) (31) Gubbens et al. (1988) (32) Moze et al. (1988) (33) Moze et al. (1993) (34) Buschow and de Mooij (35) Brabers et al. (1993) (36) Jurczyk (1990c) (37) Jurczyk (1990c)
8) Algarabel and Ibarra (1990) 9) Jurczyk et al. (1991c) 0) Haije et al. (1990)	(38) Fernando et al. (1993) (39) Jurczyk et al. (1991a)



Fig. 29. Magnetization, M, of the RCo₁₀V₂ compounds versus temperature for (upper panel) R=Ho, (middle panel) Er, and (lower panel) Y (Brabers et al. 1993).

systems suggests parallel (F) coupling of the lighter lanthanide with the Fe sublattices, and antiparallel (AF) coupling for the heavy lanthanide with the Fe sublattices. A similar situation exists for the Co compounds (fig. 29; Brabers et al. 1993). One can clearly see the compensation points for $HoCo_{10}V_2$ and $ErCo_{10}V_2$, and the obvious absence of one for YCo10V2. The change of composition does not substantially affect the magnetic parameters for the NdFe_{12-x} V_x system (H. Yang et al. 1993) (fig. 30), as observed for the Gd, Dy and Ho alloys. The $YFe_{12-x}V_x$ and $ErFe_{12-x}V_x$ systems (Pareti et al. 1991) show larger changes of the Curie points and saturation magnetization, which most likely results from the larger existence range; however, there is some doubt whether the alloys with higher x are actually single-phase systems. Figure 31 demonstrates that the Curie points are detectable in properties other than the magnetic properties (Buschow 1988b). The temperature dependence of the thermal expansion of $RFe_{10}V_2$ compounds presents anomalies at temperatures corresponding to $T_{\rm C}$'s. However, it is strange that one cannot see anomalies related to SRT. This anomaly is seen clearly in the temperature dependence of the magnetization of $DyCo_{10}V_2$ (see fig. 32, Jurczyk et al. 1991b). In contrast to the $R(Fe, Co)_{12-x}Ti_x$ alloys those with V exist for the whole concentration range (Jurczyk and Chistyakov 1989, Jurczyk et al. 1991a,b), and they correspond to the $R(Fe, Co)_{10}V_2$



Fig. 30. Curie points, $T_{\rm C}$ (circles), spinreorientation temperatures, $T_{\rm SR}$ (diamonds) and saturation magnetic moments M_s , at 1.5 K (triangles, right-hand scale) versus V concentration x for NdFe_{12-x}V_x (H. Yang et al. 1993).



Fig. 31. Relative thermal expansion, $\Delta l/l$, of the RFe₁₀V₂ compounds versus temperature above room temperature for R=Nd, Sm, Gd, Tb, Ho and Er. The anomalies in the $\Delta l/l(T)$ plot correspond to the Curie points (Buschow 1988b).



Fig. 32. Magnetization, M (in arbitrary units) versus temperature under low magnetic field, for DyFe_{10-x}Co_xV₂. For x = 10, one can see a spin-reorientation-type transition near 615 K, however the magnetization direction above this temperature is not determined. For other compositions this high-temperature transition was not detected. (Jurczyk et al. 1991b.)



Fig. 33. (i) Lattice parameters a (upper curve) and c (lower curve), (ii) Curie points, (iii) saturation magnetic moments at RT (solid circles) and LN₂ (open circles), and (iv) anisotropy fields H_A (symbols as in iii) versus Co concentration x in YFe_{10-x}Co_xV₂ alloys. The occurrence of maxima in $T_C(x)$ and $M_s(x)$ plots can be explained, as for the Slater-Pauling curve, in terms of the rigid band model in which holes are present in both 3 subbands in the Fe-rich samples. (Jurczyk and Chistyakov 1989.)



Fig. 34. (Upper panel) lattice parameters (a: circles, right-hand scale; c: triangles, left-hand scale) and (lower panel) Curie ($T_{\rm C}$) and spin-reorientation ($T_{\rm SR}$) temperatures (left-hand scale, circles), and saturation magnetization $M_{\rm s}$ at 290 K (right-hand scale, crosses) versus Co concentration x in DyFe_{10-x}Co_xV₂ alloys. Note that there are two spin-reorientation transitions below RT. The surprising spin-reorientation phenomena in DyCo₁₀V₂ [shown here by $T_{\rm SR}$ (?)] results from an M(T) plot near 615 K (see fig. 32). At present one cannot determine the phase which is formed at this temperature. (Jurczyk et al. 1991a,b.)

R	<i>a</i> (nm)	с (nm)	<i>Т</i> с (К)	M_s^M (μ_B /fu)	H _a (T)	H _{hf} (T)	Remarks	Ref.
Y	0.8463	0.4755	515			-	easy axis	1,2
				16.67ª	5.0ª		-	3
	0.8462	0.4762	514	18.8 ^b	2.6°			4
				14.9°				4
	0.8415	0.4733	525					5
Nd	0.8540	0.4771	543	13.1°	1.8°			6
	0.8556	0.4814	534	19.8 ^b	4.6°			4
				16.2°				4
Sm	0.84962	0.47599	569					7
	0.8507	0.4758	575	12.28°	5.9°		oriented powder, atomic parameters	8
Sm*				7.38°			$SmFe_{10}TiCr$: ribbon, $H_c = 0.52 T$	9
Gd	0.8515	0.4766	580				easy axis (Fe sublattice)	1,2
	0.8507	0.4769	585	1 1.2 ^b	2.7°			4
				11.3°				4
	0.8503	0.4757	580					10
Tb	0.8506	0.4757	531	9.3 ^b			easy plane (?)	4
				9.6°				4
							$T_{\rm SR} = 298 \rm K$; CEF parameters	11
	0.8502	0.4769	525				$T_{\rm SR1} = 255 \rm K, \ T_{\rm SR2} = 290 \rm K$	5
Dy	0.8492	0.4753	499	9.8 ^b	4.9°			4
				10.0°				4
							$T_{\rm SR} = 190 \rm K$; CEF parameters	11
	0.8497	0.4769	495				$T_{\rm SR1} = 75 \rm K; \ T_{\rm SR2} = 175 \rm K$	5
			608(1))		430ª	¹⁶¹ Dy ME	12
Но	0.8475	0.4725	487	9.9	4.0°			4
	0.0440		10-	10.9°			T 0.0 V	4
-	0.8448	0.4747	485	10.01			$T_{\rm SR} = 80 {\rm K}$	5
Er	0.8534	0.4761	478	10.2	2.7*			4
				11.4				4
		0 45 40					$T_{\rm SR} = 25$ K; CEF parameters	13
m	0.8426	0.4742	475	10.15	2.06		$T_{\rm SR} = 55 \mathrm{K}$	2
Im	0.8477	0.4675	400	10.1	2.8°			4
	0.0416	0.4722	165	11.0*				4
τ	0.8416	0.4732	465					5
Lu V	0.8412	0.4/30	450				VCa. Cause a substantiation and sain	5
I*							polarization calculations	14
* Va	iable com	position; se	e Rema	rks colun	ın.	b	At 77 K.	
• At	4.2 K.					c	At 293 K.	
Refer	rences							
(1) Bi	ischow et al	. (1988)		(6) Chir	1 et al. (1	989)	(11) Stefański (1990)	
(2) de	Mooij and	Buschow (1)	988)	(7) Bus	how (19	88a)	(12) Gubbens et al. (1991)	
(3) Ve	ernoef et al.	(1988) L (1980a)		(8) Oha	sni et al.	(1988a) (1990)	(13) Stefanski and Kowalczyk (1 (14) Fermanda at al. (1992)	.991)
(4) St	eranski et al	i. (1989a)		(9) UKa	ua et al.	(1990)	(14) remando et al. (1993)	

(10) Pareti et al. (1991)

Table 17 Ternary RFe₁₀Cr₂-type compounds

(5) F.-M. Yang et al. (1991)

formula. Their lattice parameters do not follow Vegard's law; however, the (a, c) vs. x plot shows a monotonic decrease with increasing x. Maxima are observed in the saturation magnetization (shifted to lower Co concentration) and the Curie points (shifted to higher concentration) as is seen in fig. 33 (Jurczyk and Chistyakov 1989) for Y pseudoternaries and in fig. 34 for Dy alloys (Jurczyk et al. 1991a,b).

3.3.1.4. Compounds with Cr. The magnetic properties of compounds with Cr are listed in table 17 which demonstrates that only compounds with Fe were obtained. All of them exhibit the RFe₁₀Cr₂ stoichiometry with Curie points between 608(1) K for the Dy compound (Gubbens et al. 1991) and 450 K for a compound of Lu (Yang et al. 1991). The comparison of saturation magnetic moments suggests that the rare-earth sublattice is coupled parallel to the Fe sublattice in the Nd compound ($19.8\mu_B/fu$ vs. $18.8\mu_B/fu$ for YFe₁₀Cr₂; Stefański et al. 1989a), while heavier lanthanide demonstrate AF coupling. Generally, the saturation magnetic moment for the compounds of heavier lanthanides is rather low. For YFe₁₀Cr₂ the magnetic moment determined at LN₂ ($18.8\mu_B/fu$ is higher than that at 4.2 K ($16.7\mu_B/fu$, Verhoef et al. 1988) and reason of this difference is not clear.

3.3.1.5. Compounds with Mn. One can see from table 18 that only alloys of $YMn_{12-x}Fe_x$ -
type, NdFe10Mn2 and SmFe10TiMn are known. Magnetic data for these are scarce and
do not exhibit any useful parameters, and that is perhaps the reason that they have not
been investigated further.

Table 19

					Ternary R	Fe_{12-x}	/n _x -type compounds	
R	x	a (nm)	c (nm)	<i>Т</i> с (К)	$M_{ m s}^{ m M}$ ($\mu_{ m B}/{ m fu}$)	Н _а (Т)	Remarks	Ref.
Y	>4	$f(\mathbf{x})$	$f(\mathbf{x})$				ND, magnetic moments at crystallographic sites	1
Nd	2.0	0.8550	0.4773	392	9.5°	1.0ª		2
Sm*					9.44ª		$SmFe_{10}TiMn$ ribbon, $H_c = 0.09 T$	3
* Var	iable c	compositi	ion; see F	Remark	s column.		^a At 293 K.	
<i>Refere</i> (1) Ya	<i>ences</i> ng et a	I. (1981)			(2) Ohashi	et al. (1	991) (3) Okada et al. (1990)	

3.3.1.6. Compounds with Mo. Data for these compounds are collected in table 19. They exhibit various stoichiometry, however, $Ce_{1.33}Fe_{8.8}Mo_{3.2}$ is quite exceptional in this group of compounds (see Berezyuk et al. 1994). The Mo compounds are formed with Fe and Co, and with both Fe and Co. Figure 6 (above) shows the lattice parameters for the RFe₁₀Mo₂ compounds (Ermolenko et al. 1990). They exhibit in principle the lanthanide contraction, however, the *a* parameter of CeFe₁₀Mo₂ is apparently lower than expected



Fig. 35. Curie points $T_{\rm C}$ (right-hand scale) and saturation magnetization $M_{\rm s}$ at 4.2 K under magnetic field of 7.2 MA/M (left-hand scale) for RFe₁₀Mo₂ compounds for various R (Ermolenko et al. 1990).

from general trend. A similar deviation is seen for the c parameters for both Ce and Pr compounds. These deviations could result from the mixed-valence state of Ce and Pr in these compounds as it was recently shown for Ce₂Fe₁₄B and related compounds by Capehart et al. (1993) in an XPS experiment. However, this problem needs further elucidation. The Curie points presented in table 19 as well as in fig. 35 (Ermolenko et al. 1990) are markedly lower (below 500 K) than that for the respective compounds with other stabilizing components. The reason is most probably the substitution of the Fe by the Mo atoms in the 8(i) position as observed by de Mooij and Buschow (1988) in the rare-earth compounds and also in uranium compounds by Suski et al. (1992b). The same explanation has been applied to relatively low $T_{\rm C}$ and $H_{\rm hf}$ observed in Ce1.33Fe8.8Mo3.2 (Berezyuk et al. 1994) but in this case the excess of Ce in relation to stoichiometric compound makes this explanation somewhat questionable. At the same time the preferential occupation of the 8(i) position by V atoms in NdFe_{12-x}V_x (Christides et al. 1990) does not noticeably decrease the magnetic properties. The saturation magnetic moments presented in fig. 35 (Ermolenko et al. 1990) confirm the conclusions presented earlier about mutual coupling of lanthanide and transition metal sublattices. The low values of magnetic moment observed for CeFe₁₀Mo₂ can confirm above suggested mixed valence state of Ce ion. The nonstoichiometric Ce1.33Fe8.8Mo3.2 exhibits higher ME magnetic moment than that determined in magnetometric measurements (Berezyuk et al. 1994) which can result from a contribution of the amorphous $Ce_{1-x}Fe_x$ phase which is not saturated at highest applied magnetic field of 5 T. The Curie points of the Co compounds

	Ref.	1,8	5	æ	4 4	n r	4 VC	9	2	7	7	œ	9	7	ر ي ا	γ ;	10	Ś	Ċ	7	11	12	13	1,8	14	2	۰. ۲	next page
- _x Mo _x -type compounds	Remarks	CFF narameter: $A_0^0 = -120 \text{ K/}a_0^2$, easy axis		ND, element position and occupancy	single phase for $x \leq 3$	$H_c = 0.26 \text{ T}(\text{ZFC,FC}), M_r = 3.23 \text{ (ZFC) and } 3.72 \text{ (FC) } \mu_B/\text{TU}$	1 - 0.22 - 1.23	$y = -0.55$, $x = 5.2$, inaginetric to 57 Fe MF		plane anisotropy		atomic positions			ND, atomic positions and occupancy	$T_{\rm SR} = 140 {\rm K}$		$H_c = 0.26 \text{ T}^{a}$ (FC, ZFC), no difference between as-cast and annealed	sample		easy axis $ c at 78 \rightarrow 293 \text{ K}$	oriented powder, atomic parameters	$SmFe_{10}TiMo ribbon, H_c = 0.41 T$	CEF parameter: $A_2^0 = -120 \text{ K}/a_0^2$, easy axis (3d)			The ME, UEF parameter: $A_2^2 = -110 \text{ M/}{40}$	COERCIVE LIEBUILINES, MAR - 0 JALA C, 1 C) 2000 105 CONTINUED ON
t(Fe, Co) ₁₂ -	H _{hf} (T)							15 64 ^d																		0	3.8	
ernary R	H _a (T)												$1.7^{\rm b}$								4.5 ^b	3.7 ^b						
Ĕ	$M_{\rm s}^{\rm M}(\mu_{\rm B}/{ m fu})$					13.0ª		08.C	0.0	20.96°	17.44 ^b		12.0 ^b			16.2 ^ª		15.0ª				10.48^{b}	7.17 ^b		9.79ª		0 03	°.U
	T _c (K) (350	ee fig. 35				260	007	د 12 see fig. 35	455			468	see fig. 35		~410	460	415		see fig. 35	463	483		400		see fig. 35	430	430
	c (nm)	mpounds 0.4707	e fig 6: 7. 5	1.0. 6. en o			e tig. 6		e fig. 6: T_c : s	0.4805		0.4802	0.4784	e fig. 6; T _c : 8			0.47877			the fig. 6; $T_{\rm C}$:	0.47996	0.4804		0.4805		se fig. 6; $T_{\rm C}$:	0.4806	
	a (nm)	Fe _{12-x} Mo _x co		· · · ·			a, c: se		a. c: se	0.8590		0.8611	0.8553	a, c: se			0.85721			a, c: se	0.86015	0.8590		0.8580		a, c: St	0.8581	
	×	ry R _{1-y} I	0.4 0	1.6			2.0		2.0	1.5		2.0	2.0	2.0	1.8	2.0	1.5	2.0		2.0	2.0	2.0		2.0	2.0	2.0	2.0	2.0
	R	Ternal	4				ല്		Ļ L	:		pN					Sm						Sm*	Gd				

	compc
Table 19	/ R(Fe, Co) _{12-x} Mo _x -type
	Ê

angle between c- and easy axis $f(T)$ 2 375 4.5° angle between c- and easy axis $f(T)$ 2 $8(n_{\circ})$ 4.0° SRT at 150 K 2 $8(n_{\circ})$ 3.0° angle between c- and easy axis $f(T)$ 2 $8(n_{\circ})$ 3.0° angle between c- and easy axis $f(T)$ 2 245 3.0° magnetic phase transitions at 95 and 150 K, order unclear 5 345 3.0° magnetic phase trans. at 22.0 K (7) 5 300 3.2° magnetic phase trans. at 22.0 K (7) 5 300 3.2° 2.5° 2.64 Am° kg; shift in hysteresis loop in ZFC and FC, $^{\circ}$ Fe ME 2 255 5.5° $M_{i} = 26.4 \text{ Am}^{\circ}$ kg; shift in hysteresis loop in ZFC and FC, $^{\circ}$ Fe ME 2 255 10.0° $M_{i} = 2.64 \text{ Am}^{\circ}$ kg; shift in hysteresis loop in ZFC and FC, $^{\circ}$ Fe ME 2 860° 3.2° $M_{i} = 2.04 \text{ Am}^{\circ}$ kg; FC: $H_{i} = 0.24 \text{ T}$ $M_{i} = 27.0 \text{ Am}^{\circ}$ kg; FC: $H_{i} = 0.24 \text{ T}$ $M_{i} = 27.0 \text{ Am}^{\circ}$ kg; FC: $H_{i} = 0.24 \text{ T}$ $M_{i} = 27.0 \text{ Am}^{\circ}$ kg; FC: $H_{i} = 0.24 \text{ T}$ $M_{i} = 27.0 \text{ Am}^{\circ}$ kg; FC: $H_{i} = 0.24 \text{ T}$ $M_{i} = 27.0 \text{ Am}^{\circ}$ kg; FC: $H_{i} = 0.24 \text{ T}$ $M_{i} = 27.0 \text{ Am}^{\circ}$	L)	a (m)	с (пт)	$\begin{array}{c} T_{\mathrm{C}} \\ (\mathbf{K}) \end{array}$	$M_{ m s}^{ m M}(\mu_{ m B}/{ m fu})$	H _a (T)	$\stackrel{H_{\mathrm{hf}}}{(\mathrm{T})}$	Remarks	Ref.
æ fig. 35 angle between c- and easy axis $f(T)$ 2 360 4.0 ^a SRT at 150 K 2 360 4.0 ^a SRT at 150 K 5 365 5.6 s.c., c-easy axis at 4.2 \rightarrow 200 K 150 K, order unclear 5 345 3.0 ^a angle between c- and easy axis $f(T)$ 16 300 3.2 ^a magnetic phase transitions at 95 and 150 K, order unclear 5 angle between c- and easy axis $f(T)$ ND, $T_{ss} = 58(2)$ K, axial (HT) - cone (plane, LT) 16 300 3.2 ^a magn. phase trans. at 220 K (?) 5 angle between c- and easy axis $f(T)$ order unclear 5 angle between c- and easy axis $f(T)$ order unclear 5 300 3.2 ^a magn. phase trans. at 220 K (?) 5 angle between c- and easy axis $f(T)$ order unclear 5 ang. $f_{T} = -32.7^{a}$ $M_{T} = -32.7^{a}$ $M_{T} = -32.7^{a}$ ang. $f_{T} = -32.8$ $M_{T} = -20.3 T^{a}$ $M_{T} = -27.0 Am^{2}/R_{S}$ $f_{T} = -355$ 10^{a} $M_{T} = -26.4 Am^{2}/R_{S}$ $M_{T} = -2.2.8 Am^{2}/R_{T}$ $M_{T} = -27.0 Am^{2}/R_{S}$ <t< td=""><td>a, c: see fig. 6; $T_{\rm C}$</td><td>: fig. 6; T_c</td><td>Set</td><td>e fig. 35 375</td><td>4.5ª</td><td></td><td></td><td>angle between c- and easy axis $f(T)$ possibility of smooth SRT</td><td>N 5</td></t<>	a, c : see fig. 6; $T_{\rm C}$: fig. 6; T _c	Set	e fig. 35 375	4.5ª			angle between c - and easy axis $f(T)$ possibility of smooth SRT	N 5
360 4.0^a SRT at 150K 5 ac fig. 35 3.0^a magnetic phase transitions at 95 and 150 K, order unclear 5 345 3.0^a magnetic phase transitions at 95 and 150 K, order unclear 5 300 3.2^a magnetic phase transitions at 95 and 150 K, order unclear 5 300 3.2^a magnetic phase trans. at 220 K (?) 5 300 3.2^a magnetic phase trans. at 220 K (?) 5 angle between c- and easy axis $f(T)$ - cone (plane, LT) 16 300 3.2^a magn. phase trans. at 220 K (?) 5 285 5.5^a ZFC: $H_c = 0.32 T^a$, $M_r = 22.8 Am^3/kg$; FC: $H_c = 0.32 T^a$, $M_r = 2.64 Am^3/kg$; FC: $H_c = 0.24 T$, $M_r = 2.70 Am^2/kg$; 5 2 255 10.0^a ZFC: $H_c = 0.15 T$, $M_r = 17.0 Am^2/kg$; FC: $H_r = 0.24 T$, $M_r = 27.0 Am^2/kg$; 5 2 255 10.0^a ZFC: $H_c = 0.15 T$, $M_r = 17.0 Am^2/kg$; FC: $H_r = 0.24 T$, $M_r = 27.0 Am^2/kg$; 5 2 256 1.7^a axial anisotropy 2 2 257 10.0^a 2.0^a Am^2/kg; FC: $H_r = 0.24 T$, $M_r = 27.0 Am^2/kg$; 5 2 258 1.7^a 2.0^a Am^2/kg; 7	a, c : see fig. 6; T_c :	: fig. 6; T _c :	se	e fig. 35				angle between c - and easy axis $f(T)$	5
e fig. 35 s.c., c-easy axis at $4.2 \rightarrow 200 \text{ K}$ 15 345 3.0 ^a magnetic phase transitions at 95 and 150 K, order unclear 5 360 3.2 ^a magnetic phase transitions at 320 K (7) 2 300 3.2 ^a magne between c- and easy axis $f(T)$ 2 300 3.2 ^a magne phase trans at 220 K (7) 5 300 3.2 ^a ND, $T_{ss} = 58(2) \text{ K, axial (HT) - cone (plane, LT)} 5 300 3.2a magn. phase trans. at 220 K (7) 5 285 5.5.4 Mf = 26.4 Am3/kg; shift in hysteresis loop in ZFC and FC, T_{e} = 0.32 T^{a}, 5 285 10.0a ZFC: H_{e} = 0.15 T, M_{e} = 17.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{f} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{f} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 \text{ Am}^{3}/kg; FC: H_{e} = 0.24 T, M_{e} = 27.0 A$				360	4.0ª			SRT at 150 K	S
345 3.0^{a} s.c., c-easy axis at $4.2 \rightarrow 200$ K 15 afg. 35 3.0^{a} magnetic phase transitions at 95 and 150 K, order unclear 5 300 3.2^{a} magnetic phase trans. at 220 K (?) 2 300 3.2^{a} ND, $7_{ss} = 58(2)$ K, axial (HT) - cone (plane, LT) 16 300 3.2^{a} ND, $7_{ss} = 58(2)$ K, axial (HT) - cone (plane, LT) 5 285 5.5^{a} ZFC: $H_{c} = 0.32$ T ^a , $M_{r} = 22.8$ Am ² /kg; FC: $H_{c} = 0.32$ T ^a , $M_{r} = 22.8$ Am ² /kg; FC: $H_{c} = 0.24$ T, $M_{r} = 27.0$ Am ² /kg; 5 2 255 10.0^{a} ZFC: $H_{c} = 0.15$ T, $M_{r} = 17.0$ Am ² /kg; FC: $H_{c} = 0.24$ T, $M_{r} = 27.0$ Am ² /kg; 5 2 255 10.0^{a} ZFC: $H_{c} = 0.15$ T, $M_{r} = 2.2.8$ Am ² /kg; FC: $H_{c} = 0.24$ T, $M_{r} = 27.0$ Am ² /kg; 5 2 590 6.4^{b} 1.64^{f} axial anisotropy 2 555 10.0^{a} 2.75^{b} 3.1^{b} axial anisotropy 17 550 6.4^{b} 3.4^{b} axial anisotropy 2 17 550 8.64^{b} 3.4^{b} axial anisotropy 17 555 2.56^{b} <td< td=""><td>a, c: see fig. 6; T_c:</td><td>: fig. 6; $T_{\rm C}$:</td><td>se</td><td>e fig. 35</td><td></td><td></td><td></td><td></td><td>7</td></td<>	a, c : see fig. 6; T_c :	: fig. 6; $T_{\rm C}$:	se	e fig. 35					7
345 3.0^{a} magnetic phase transitions at 95 and 150 K, order unclear 5 angle between c- and easy axis $f(T)$ 166 300 3.2^{a} magnetic phase transitions at 200 K (?) 2 300 3.2^{a} ND, $T_{ss} = 58(2)$ K, axial (HT) - cone (plane, LT) 5 86 fig. 35 5.5^{a} ZFC: $H_{e} = 0.32 T^{a}$, $M_{f} = 22.8 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.32 T^{a}$, $M_{f} = 26.4 \text{Am}^{2} \text{kg}$; shift in hysteresis loop in ZFC and FC, T_{T} PME 2 255 10.0^{a} ZFC: $H_{e} = 0.15 T$, $M_{f} = 17.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{f} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{f} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{f} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{f} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{f} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{f} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{f} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{f} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; FC: $H_{e} = 0.24 \text{T}$, $M_{e} = 27.0 \text{Am}^{2} \text{kg}$; F								s.c., <i>c</i> -easy axis at $4.2 \rightarrow 200 \text{ K}$	15
e fig. 35 angle between c- and easy axis $f(T)$ 2 300 3.2^{a} ND, $T_{ss} = 58(2)$ K, axial (HT) - cone (plane, LT) 16 300 3.2^{a} ND, $T_{ss} = 58(2)$ K, axial (HT) - cone (plane, LT) 2 285 5.5^{a} ZFC: $H_{c} = 0.32$ T ^a , $M_{r} = 22.8 \text{ Am}^{2}/\text{kg}$; FC: $H_{c} = 0.32$ T ^a , $M_{r} = 26.4 \text{ Am}^{2}/\text{kg}$; shift in hysteresis loop in ZFC and FC, 97 Fe MB 2 255 10.0^{a} ZFC: $H_{c} = 0.15$ T, $M_{r} = 17.0 \text{ Am}^{2}/\text{kg}$; FC: $H_{c} = 0.24$ T, $M_{r} = 27.0 \text{ Am}^{2}/\text{kg}$; S 2 86 6.4^{b} 1.64^{f} axial anisotropy 2 575 7.6^{b} 1.7^{b} axial anisotropy 17 575 7.6^{b} 1.7^{b} axial anisotropy 17 526 8.37^{b} 3.4^{b} axial anisotropy 17 525 2.0^{b} 2.0^{b} 2.0^{b} 2.0^{b} 17 526 $4.1.7^{b}$ axial anisotropy 7.6^{c} 7.6^{c} 17 526 $4.2.7^{b}$ 4.8^{b} 2.0^{b} 2.0^{b} 2.0^{b} 17 520 8.64^{b} 3.4				345	3.0ª			magnetic phase transitions at 95 and 150 K, order unclear	Ś
300 3.2^a ND, $T_{Rs} = 58(2)$ K, axial (HT) - cone (plane, LT) 16 300 3.2^a magn. phase trans. at 220 K (?) 5 285 5.5^a ZFC: $H_c = 0.32$ T ^a , $M_r = 22.8$ Am ² /kg; FC: $H_r = 0.32$ T ^a , $M_r = 26.4$ Am ² /kg; FC: $H_r = 0.32$ T ^a , $M_r = 26.4$ Am ² /kg; FC: $H_r = 0.24$ T, $M_r = 27.0$ Am ² /kg; FC: $H_r = 0.24$ T, $M_r = 0.24$ T, $M_r = 0.24$ T,	a, c : see fig. 6; T_c : s	: fig. 6; T _C : s	ĕ	e fig. 35				angle between c - and easy axis $f(T)$	7
300 3.2^{a} magn. phase trans. at 220 K (?) 5 285 5.5^{a} ZFC: $H_{c} = 0.32 T^{a}$, $M_{r} = 22.8 \text{ Am}^{2}/\text{kg}$; FC: $H_{c} = 0.32 T^{a}$, 5 285 5.5^{a} ZFC: $H_{c} = 0.32 T^{a}$, $M_{r} = 22.8 \text{ Am}^{2}/\text{kg}$; FC: $H_{c} = 0.32 T^{a}$, 2 255 10.0^{a} ZFC: $H_{c} = 0.15 T$, $M_{r} = 17.0 \text{ Am}^{2}/\text{kg}$; FC: $H_{c} = 0.24 T$, $M_{r} = 27.0 \text{ Am}^{2}/\text{kg}$; 5 256 4^{a} 2^{c} stial anisotropy 17 390 6.4^{b} 1.64^{f} axial anisotropy 17 575 7.6^{b} 1.7^{b} axial anisotropy 17 575 7.6^{b} 1.7^{b} axial anisotropy 17 575 7.6^{b} 1.7^{b} axial anisotropy 17 575 8.4^{b} 3.4^{b} axial anisotropy 17 500 2.36^{b} 2.0^{b} 2.0^{b} 2.0^{b} 17 575 4.50^{b} 2.0^{b} 2.0^{b} 3.1^{b}	0.85015(5) 0.47759(3)	0.47759(3)	_					ND, $T_{SR} = 58(2)$ K, axial (HT) – cone (plane, LT)	16
e fig. 35 25.a $ZFC: H_c = 0.32 T^a, M_r = 22.8 Am^2/kg; FC: H_c = 0.32 T^a, M_r = 22.8 Am^2/kg; FC: H_c = 0.32 T^a, M_r = 22.8 Am^2/kg; FC: H_r = 0.32 T^a, M_r = 27.0 Am^2/kg; FC: H_r = 0.24 T, M_r = 0.24 T, M_r = 0.04 T, M_r = 0.04 T, M_r = 0.04 T, M_r = 0.04 M_{103}, T_{cm} = 60 K$ 17 540 2.0 b 2.10 b				300	3.2ª			magn. phase trans. at 220 K (?)	S
285 5.5 ^a ZFC: $H_c = 0.32 T^a$, $M_r = 22.8 \text{ Am}^3/\text{kg}$; FC: $H_c = 0.32 T^a$, 5 5 8c fig. 35 $M_r = 26.4 \text{ Am}^2/\text{kg}$; shift in hysteresis loop in ZFC and FC, ^{77}Fe ME 2 255 10.0^a ZFC: $H_c = 0.15 \text{ T}$, $M_r = 17.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.24 \text{ T}$, $M_r = 27.0 \text{ Am}^2/\text{ Am}^2/\text{ Am}^2/\text{ Am}^2/\text{ Am}^2/\text{ Am}^2/\text{ Am}^2/Am$	a, c : see fig. 6; T_c :	: fig. 6; T _c :	šč	e fig. 35					7
æ fig. 35 255 10.0^{a} ZFC: $H_{c} = 0.15$ T, $M_{r} = 17.0$ Am ² /kg; FC: $H_{c} = 0.24$ T, $M_{r} = 27.0$ Am ² /kg; 5 259 6.4^{b} 1.64^{f} axial anisotropy 270 5.20^{b} $Y_{1.03}$ Co ₁₀ Mo _{1.94} 275 7.6^{b} 1.7^{b} axial anisotropy 252 7.25^{b} 3.1^{b} axial anisotropy 252 7.25^{b} 3.1^{b} axial anisotropy 252 8.37^{b} 3.1^{b} axial anisotropy 253 8.54^{b} 3.4^{b} axial anisotropy 250 8.64^{b} 3.4^{b} axial anisotropy 250 8.64^{b} 3.4^{b} axial anisotropy 250 8.64^{b} 3.4^{b} axial anisotropy 250 8.64^{b} 3.4^{b} axial anisotropy 260 2.36^{b} 2.0^{b} Gd_{103} Co ₁₀ Mo _{1.94} . $T_{cm} = 60$ K 710 2.98^{b} Y_{10} Zo_{10} Mo _{1.94} . $T_{cm} = 60$ K 730 4.1^{b} Y_{10} Y_{103} Co ₁₀ Mo _{1.94} . $T_{cm} = 60$ K 730 4.1^{b} Y_{10} Y_{103} Co ₁₀ Mo _{1.94} . $Y_{cm} = 60$ K 730 4.1^{b} Y_{10} Y_{103} Y_{103} $Y_{cm} = 60$ K 730 4.1^{b} Y_{10} Y_{103} Y_{103} Y_{10} Y_{10				285	5.5 ^a			ZFC: $H_c = 0.32 T^a$, $M_r = 22.8 \text{ Am}^2/\text{kg}$; FC: $H_c = 0.32 T^a$, $M_r = 26.4 \text{ Am}^2/\text{kg}$: shift in hysteresis loop in ZFC and FC. ⁵⁷ Fe ME	S
255 10.0^{a} ZFC: $H_{c} = 0.15T$, $M_{r} = 17.0 \mathrm{Am}^{2}/\mathrm{kg}$; FC: $H_{c} = 0.24 \mathrm{T}$, $M_{r} = 27.0 \mathrm{Am}^{2}/\mathrm{kg}$; 5590 6.4^{b} 1.64^{f} axial anisotropy 17 575 7.6^{b} 1.7^{b} axial anisotropy 17 575 7.6^{b} 1.7^{b} axial anisotropy 17 520 8.64^{b} 3.4^{b} axial anisotropy 17 521 7.6^{b} 1.7^{b} axial anisotropy 17 520 8.64^{b} 3.4^{b} axial anisotropy 17 600 2.36^{b} 2.0^{b} $0.0^{0}_{1.03}$ $T_{cm} = 60 \mathrm{K}$ 17 530 4.27^{b} 4.8^{b} axial anisotropy 17 600 2.98^{b} $Dy_{1.03}C_{0,0}M_{0,194}$ $T_{cm} = 60 \mathrm{K}$ 17 600 2.98^{b} $Dy_{1.03}C_{0,0}M_{0,194}$ $T_{cm} = 60 \mathrm{K}$ 18 730 4.1^{b} $H0_{1.02}C_{0,0}M_{0,194}$ $T_{cm} = 60 \mathrm{K}$ 18	a, c : see fig. 6; T_c :	: fig. 6; T _C : 3	ĕ	e fig. 35					7
590 6.4^{h} 1.64^{f} axial anisotropy470 5.20^{h} $Y_{103}Co_{10}Mo_{1.34}$ 17575 7.6^{h} 1.7^{h} axial anisotropy18526 7.5^{h} 1.7^{h} axial anisotropy17520 8.64^{h} 3.4^{h} axial anisotropy17520 8.64^{h} 3.4^{h} axial anisotropy17520 8.37^{h} planar anisotropy17521 2.0^{h} 2.0^{h} $axial anisotropy175228.37^{h}planar anisotropy175324.50^{h}2.0^{h}axial anisotropy175402.0^{h}axial anisotropy185404.27^{h}4.8^{h}axial anisotropy6002.98^{h}Dy_{1.03}Co_{10}Mo_{1.94}T_{cm} = 60 \text{ K}187304.1^{h}H0_{1.03}Co_{10}Mo_{1.94}T_{cm} = 60 \text{ K}18$))) 1		255	10.0ª			ZFC: $H_c = 0.15$ T, $M_t = 17.0$ Am ² /kg; FC: $H_c = 0.24$ T, $M_t = 27.0$ Am ² /kg; shift in hysteresis in FC and ZFC	S
590 6.4^{b} 1.64^{f} axial anisotropy 17 470 5.20^{b} 1.7^{b} $Y_{1.03}^{\text{c}}\text{Co}_{10}\text{Mo}_{1.44}$ 18 575 7.6^{b} 1.7^{b} axial anisotropy 17 525 7.25^{b} 3.1^{b} axial anisotropy 17 520 8.64^{b} 3.4^{b} axial anisotropy 17 520 2.36^{b} 2.0^{b} axial anisotropy 17 530 2.36^{b} 2.0^{b} axial anisotropy 17 540 4.27^{b} 4.8^{b} axial anisotropy 18 600 2.98^{b} Dy _{1.03} Co _{1.0} Mo _{1.94} $7_{\text{cm}} = 60 \text{ K}$ 18 730 4.1^{b} axial anisotropy 18 17) _{12-x} Mo _x compounds	spuno							
4705.20 ^b $Y_{103}Co_{10}Mo_{1,34}$ 185757.6 ^b 1.7 ^b axial anisotropy175257.25 ^b 3.1 ^b axial anisotropy175208.64 ^b 3.4 ^b axial anisotropy175954.50 ^b 2.0 ^b axial anisotropy175962.36 ^b Cd ₁₀₃ Co ₁₀ Mo _{1,94} , T _{cm} = 60 K186002.98 ^b Dy ₁₀₃ Co ₁₀ Mo _{1,94} , T _{cm} = 60 K187304.1 ^b Ho ₁₀₃ Co ₁₀ Mo _{1,94} 8	0.8426 0.4722	0.4722		590	6.4 ^b	1.64 ^f		axial anisotropy	17
5757.6 ^b 1.7 ^b axial anisotropy175257.25 ^b 3.1 ^b axial anisotropy175208.64 ^b 3.4 ^b axial anisotropy176258.37 ^b 2.0 ^b axial anisotropy175954.50 ^b 2.0 ^b axial anisotropy179502.36 ^b Cd ₁₀₃ Co ₁₀ Mo ₁₃₄ , $T_{cm} = 60$ K185404.27 ^b 4.8 ^b axial anisotropy186002.98 ^b Dy ₁₀₃ Co ₁₀ Mo ₁₃₄ , $T_{cm} = 60$ K187304.1 ^b Ho ₁₀₃ Co ₁₀ Mo ₁₃₄ , $T_{cm} = 60$ K18	0.8421(1) 0.4720(1)	0.4720(1)		470	5.20 ^b			Y ₁₀₃ Co ₁₀ Mo _{1.94}	18
5257.25^b3.1 baxial anisotropy175208.64^b3.4 baxial anisotropy176258.37 b2.0 baxial anisotropy175954.50^b2.0 baxial anisotropy179502.36^bGd ₁₀₃ CO ₁₀ MO _{1,94} , $T_{cm} = 60$ K185404.27^b4.8 baxial anisotropy186002.98^bDy ₁₀₃ CO ₁₀ MO _{1,94} , $T_{cm} = 60$ K187304.1 bHO ₁₀₃ CO ₁₀ MO _{1,94} , $T_{cm} = 60$ K18	0.8414 0.4718	0.4718		575	7.6 ^b	1.7 ^b		axial anisotropy	17
5208.64 ^b 3.4 ^b axial anisotropy176258.37 ^b planar anisotropy175954.50 ^b 2.0 ^b axial anisotropy179502.36 ^b Gd ₁₀₃ CO ₁₀ MO _{1,94} , $T_{cm} = 60$ K187404.27 ^b 4.8 ^b axial anisotropy186002.98 ^b Dy ₁₀₃ CO ₁₀ MO _{1,94} , $T_{cm} = 60$ K187304.1 ^b HO ₁₀₃ CO ₁₀ MO _{1,94} , $T_{cm} = 60$ K18	0.8478 0.4733	0.4733		525	7.25 ^b	3.1 ^b		axial anisotropy	17
625 8.37^{b} planar anisotropy 17 595 4.50^{b} 2.0^{b} axial anisotropy 17 950 2.36^{b} $Cd_{1.03}CO_{10}MO_{1.94}, T_{cm} = 60 K$ 18 850 2.36^{b} $Cd_{1.03}CO_{10}MO_{1.94}, T_{cm} = 60 K$ 18 8540 4.27^{b} 4.8^{b} axial anisotropy 18 600 2.98^{b} $Dy_{1.03}CO_{10}MO_{1.94}, T_{cm} = 60 K$ 18 730 4.1^{b} $Ho_{1.03}CO_{10}MO_{1.94}, T_{cm} = 60 K$ 18	0.8475 0.4736	0.4736		520	8.64 ^b	3.4 ^b		axial anisotropy	17
595 4.50^b 2.0^b axial anisotropy 17 950 2.36^b $Gd_{1.03}CO_{10}MO_{1.34}, T_{cm} = 60$ K 18 740 4.27^b 4.8^b axial anisotropy 18 600 2.98^b $Dy_{1.03}CO_{10}MO_{1.34}, T_{cm} = 60$ K 18 730 4.1^b $Ho_{1.03}CO_{10}MO_{1.34}, T_{cm} = 60$ K 18	0.8440 0.4723	0.4723		625	8.37 ^b			planar anisotropy	17
950 2.36^{b} $Gd_{1.03}CO_{10}MO_{1.34}$, $T_{cm} = 60$ K 18 740 4.27^{b} $Tb_{1.03}CO_{10}MO_{1.34}$, $T_{cm} = 60$ K 18 600 2.98^{b} $Dy_{1.03}CO_{10}MO_{1.34}$, $T_{cm} = 60$ K 18 730 4.1^{b} $Ho_{1.03}Co_{10}MO_{1.34}$, $T_{cm} = 60$ K 18	0.8438 0.4726	0.4726		595	4.50 ^b	2.0 ^b		axial anisotropy	17
Tb ₁₀₃ Co ₁₀ Mo _{1,94} Tb ₁₀₃ Co ₁₀ Mo _{1,94} 18 540 4.27^{b} axial anisotropy 17 600 2.98^{b} Dy ₁₀₃ Co ₁₀ Mo _{1,94} , $T_{\text{cm}} = 60 \text{ K}$ 18 730 4.1^{b} Ho ₁₀₃ Co ₁₀ Mo _{1,94} , $T_{\text{cm}} = 60 \text{ K}$ 18	0.8441(2) 0.4740(2)	0.4740(2)		950	2.36 ^b			$Gd_{1,03}Co_{10}Mo_{1,94}, T_{cm} = 60 K$	18
540 $4.27^{\rm b}$ $4.8^{\rm b}$ axial anisotropy17600 $2.98^{\rm b}$ $Dy_{1.03}CO_{10}MO_{1.94}, T_{cm} = 60 {\rm K}$ 18730 $4.1^{\rm b}$ ${\rm Ho}_{1.03}CO_{10}MO_{1.94}$ 18	0.8414(4) 0.4710(3)	0.4710(3)	_					Tb _{1.03} Co ₁₀ Mo _{1.94}	18
600 2.98^{b} $Dy_{1.03} Co_{10} Mo_{1.94}, T_{cm} = 60 K$ 18 730 4.1^{b} $Ho_{1.03} Co_{10} Mo_{1.94}$ 18	0.8423 0.4721	0.4721		540	4.27 ^b	4.8 ^b		axial anisotropy	17
730 4.1 ^b Ho ₁₀₃ Co ₁₀ Mo _{1,34} 18	0.8415(5) 0.4707(5)	0.4707(5)	_	600	2.98 ^b			$Dy_{1.03} Co_{10} Mo_{1.94}, T_{cm} = 60 K$	18
	0.8411(2) 0.4716(2)	0.4716(2)		730	4.1 ^b			H01.03 C010 M01.34	18

Table 19, continued

						Table 19	, continued		
R x	a (mn)	с (пп)	$\begin{array}{c} T_{\rm c} \\ ({\rm K}) \end{array}$	$M_{ m s}^{ m M}$ ($\mu_{ m b}/{ m fu}$)	H _a (T)	$H_{\rm hf}$ (T)	Remarks		Ref.
Er 2.0	0.8400	8.4715 0.4700753	570 675	6.98 ^b 5 40 ^b	1.2 ^b		$T_{\text{SRI}} = 140 \text{ K}, T_{\text{SR2}} = 350 \text{ K}$, cone between T_{SRI}	and $T_{ m SR2}$	17
Tm	0.8397(2)	0.4709(2)	500	4.0 ^b			$Tm_{1,03}CO_{10}MO_{1,94}$, $T_{em} = 20$ Tm_{1,03}CO_{10}MO_{1,94}, $T_{em} = 15$ K		18
Lu Y*	0.8367(2)	0.4685(2)	830 <i>f(y</i>)	5.25 ^b			Lu _{1.05} Co ₁₀ Mo _{1,94} Y(Fe _{1-y} Co _y) _{12-x} Mo _x , $y = 0, 3, 5, 7, 10.5, x = 1.$ diagram	.5: T_{SR} vs. y , magn. phase	18 19
*PN			f(x)	f(x)			NdFe _{102-x} Co _x Mo _{1.8} : $H_{\rm er}$ of FOMP vs. x, $T_{\rm SR12}$	2 VS. X	17,20 5
ыт. Но *			490				SILUE $G_{0,2}(MO_2)$: $H_c = 0.061$ at $3 \mathbb{N}$ HoFe _{10-x} Co _x MO ₂ , $0 \le x \le 8$: s.c. and polycrys no SRT	tt, easy axis at $4.2 \rightarrow 300 \mathrm{K}$	د 15
Er*	f(x)	f(x)	$f(\mathbf{x})$	1		i	$\operatorname{ErFe}_{10.5-x}\operatorname{Co}_{x}\operatorname{Mo}_{1.5}: T_{\operatorname{SR}1,2} \operatorname{vs.} x$		20
* Variable com ^a At 4.2 K. ^b At 293 K.	position; see Rei	marks column.		^c In µ _B /F ^d At 13 F	Fe atom. C.		° At 1.5 K. ¹ At 77 K.		
References (1) Buschow el (2) Ermolenko (3) Tomey et al (4) Geng et al. (5) Christides (t al. (1988) et al. (1990) 1. (1993) (1991) 1. al. (1993)	(6) (7) (9) (9) (10)	Berezyu Yang et de Mooi Chin et (Buscho	k et al. (199 al. (1992) ij and Busch al. (1989) w (1988a)	94) how (1988	e	(11) J. Hu et al. (1989) (16) To (12) Ohashi et al. (1988a) (17) Xi (13) Okada et al. (1990) (18) Be (14) Verhoef et al. (1988) (19) Ga (15) Scherbakova et al. (1993) (20) Lu	mey et al. (1994) ie Xu and Shaheen (1993b) srezyuk et al. (1995) rreia et al. (1994) uis et al. (1994)	





Fig. 36b. Magnetic phase diagram (T, x) for the alloys of fig. 36a. Lines in the phase diagram are guides for the eye. (Luis et al. 1994.)



are higher than those of the Fe compounds, as usual in these types of compounds (Xie Xu and Shaheen 1993a), however, their dependence on the atomic number of lanthanide is irregular. At the same time the values of magnetic moment are markedly lower than that for Fe compounds but in principle confirm a general rule of the coupling between the Co and lanthanide sublattices. Only the high value of the observed magnetic moment for $ErCo_{10}Mo_2$ breaks this regularity (Xie Xu and Shaheen 1993a). The conical magnetic structure is different from that of other compounds, and this might be the cause of this discrepancy.

Pseudoternary alloys of Fe and Co are known for Y, Nd, Ho and Er (see table 19). Their lattice parameters do not obey Vegard's law but a smooth change of both parameters is observed with a change of concentration (see fig. 36 after Luis et al. 1994 for Nd alloys and fig. 37 after Garcia et al. 1994 for Er alloys). The Mo index is usually lower than 2 except for the Ho pseudoternaries (Scherbakova et al. 1993). One can see from fig. 38 (Garcia et al. 1994) that in the $YFe_{10.5-x}Co_xMo_{1.5}$ system the spin-reorientation transition from the cone to the axial magnetic structure occurs for 2.5 < x < 8.5. This is quite a unique behavior, however. The recent interest in the 3d anisotropy in the rare-earth-transition-element intermetallics has revealed many unusual properties (Thuy 1994, private communication). The Curie points in these systems increase with increasing Co concentration (Garcia et al. 1994). In turn Nd (Luis et al. 1994) and Er (Garcia et al. 1994) alloys exhibit a maximal value of T_C for x=7 for both systems (see figs. 35 and 37, respectively). The saturation magnetization at RT shows a monotonous decrease with increasing x for Nd compounds (Luis et al. 1994), and a maximum for ErFe_{5.5}Co_{5.0}Mo_{1.5}



Fig. 37. (Lower panel) magnetic phase diagram (x, T), and (upper panel) lattice parameters (a, open circles; c, solid circles) and saturation magnetization M_s at RT (open triangles) versus Co concentration x in $\text{ErFe}_{10.5-x}\text{Co}_x\text{Mo}_2$ alloys (Garcia et al. 1994). Lines in the magnetic phase diagram are guides to the eye.

Fig. 38. Magnetic phase diagram (T, x) for $YFe_{10.5-x}Co_xMo_{1.5}$ (Garcia et al. 1994).

(Garcia et al. 1994). One should remember that optimizing of $T_{\rm C}$ and $M_{\rm s}$ is not enough for selecting the proper magnetic material, because still one should consider the remanence and coercive field.



Fig. 39. (Lower panel) Curie points $T_{\rm C}$ and spin-reorientation temperatures $T_{\rm SR}$, and (upper panel) lattice parameters (*a*, left-hand scale, circles; *c*, right-hand scale, triangles) versus Co concentration *x* in TbFe_{10.8-x}Co_xW₂ alloys (Jurczyk and Rao 1991).

3.3.1.7. Compounds with W. The data for compounds with W are presented in table 20. There are only few such materials (alloys of Y, Sm Gd and Tb) with W concentration less than 2. The alloys with Co and Ni are not known but the pseudoternaries with Fe and Co are represented by alloys of Y and Tb. The Curie points of the Fe ternaries are between 500 and 570 K, and the difference in saturation magnetization between the Y and Gd compounds seems to suggest AF coupling between the Gd and Fe sublattices.

In TbFe_{10.8-x}Co_xW_{1.2} (fig. 39, Jurczyk and Rao 1991) the existence range corresponds to $0 \le x \le 5$. Figure 39 shows that the $T_{\rm C}$ increases with increasing Co concentration, but the saturation magnetization has not been reported.

3.3.1.8. Compounds with Re. Surprisingly, the alloys with Re, in spite of the relative rarity of this stabilizing component, have been broadly investigated. Their lattice parameters and magnetic data are collected in table 21. In this group there are representatives of materials in which the lanthanide atom is overstoichiometric relative to the normal formula $RT_{12-x}M_x$, and the excess lanthanide atoms are most probably located at other than the 2(a) sites (Berezyuk et al. 1994). For these alloys, as a rule, the magnetic moment per Fe atom determined from ⁵⁷Fe Mössbauer experiments is lower than that estimated from magnetometric measurements. This suggests parallel coupling between the sublattices of the lanthanide and iron. However, the values are not accurate due to

					Terr	ıary RFe	Table 2 2 _{12-x} W _x -t	20 ype compounds	
ж	×	a (mn)	с (пп)	<i>T</i> _c (K)	$M_{\rm s}$ ($\mu_{\rm B}/{ m fu}$)	H _a (T)	$H_{\rm hf}$ (T)	Remarks	Ref.
¥	1.2	0.8548	0.4779	500				easy axis	1,2
	1.2 1.2			510	20.58 ⁴ 19.8 ⁶	5.0ª 5.5 ^b		easy axis	ro 4
					16.4°	3.4°			4
	1.2						26.9 ^b	⁵⁷ Fe ME	5
Sm	1.5	0.85572	0.47912	520					9
Gd	1.2	0.8549	0.4773	570				easy axis	1,2
					15.32 ^a	7.0ª			÷
	1.2	0.8565	0.4777	550			12.8ª	⁵⁷ Fe ME, CEF parameter: $A_2^0 = -140 \text{ K}/a_2^0$	7
	1.2						27.1 ^b	⁵⁷ Fe ME	5
Υ .								$Y(Fe_{1-x}Co_x)_{10.8}W_{1.2}$	4
Tb*	*	f(x)	$f(\mathbf{x})$	f(x)				TbFe _{10.8-x} Co _x $W_{1,2}$, $0 \le x \le 5$; T_{sR} vs. x	80
* Variał ^a At 4.2	ole compe K.	osition; see R	emarks colum					^b At 77 K. ^c At 293 K.	
Referen (1) Buscl (2) de M (3) Verho	<i>ces</i> how et al. ooij and B vef et al. ((1988) huschow (1988) 1988)		(5 (5 (6) Jurczyk (1) Sinnemann) Buschow (990b) I et al. (1 ⁽ 1988a)	(9686	(7) Dirken et al. (1989) (8) Jurczyk and Rao (1991)	

R	x	<i>a</i> (nm)	c (nm)	<i>Т</i> с (К)	$M_{ m s}^{ m M}$ $(\mu_{ m B}/{ m fu})$	Н _а (Т)	H _{hf} (T)	Remarks	Ref.
Y	2.0	0.85278(10)	0.47536(10)	370	17.1 ª	1.62ª			1
	1.2	0.8529	0.4763	460	19.7°	2.5°		axial anisotropy	2
Ce	2.0	0.8562(2)	0.4745(2)	353	1 4.8 ª				1
				350	16.92ª			$Ce_{1.33}Fe_{10}Re_{2}$	3
				345	1.69 ^d		18.85°	⁵⁷ Fe ME	3
							1.3 ^{d,e}		3
Pr	*	0.86203(5)	0.47622(4)	397	16.0ª			PrFe _{10.52} Re _{1.48}	1
				50	3.98ª			Pr _{1.64} Fe _{7.2} Re _{4.8} , magn.	3
					0.55 d		7.0°	⁵⁷ Fe ME	3
							0.48 ^{d,e}		3
Nd	2.0	0.85986(4)	0.47589(5)	428(10)	21.4ª				1
Sm	2.0	0.8568(2)	0.4761(1)	475	17.0ª				1
				476	22.83 ª			Sm _{1.2} Fe _{7.5} Re _{4.5} , magn.	3
				480	3.04 ^d		6.8°	⁵⁷ Fe ME	3
							0.46 ^{d,e}		3
Gd	1.40(4)	0.85579(3)	0.47589(2)	470(10)	12.1 ª				1
Tb	2.0	0.85265(5)	0.47557(7)	438	9.2 ª				1
	1.2	0.8542	0.4765	475	12.9°			planar anisotropy	2
Dy	2.0	0.85181(10)	0.47510(11)	415(10)	8.0ª				1
Но	2.0	0.85027(9)	0.4750(1)	388(10)	9.5ª				1
	1.2	0.8511	0.4754	448(10)	11.6°	2.3 ^b		axial anisotropy	2
					12.7 ^b				2
Er	2.0	0.8485(1)	0.4751(2)	375(10)	11.5ª				1
Tm	2.0	0.84778(6)	0.47455(7)	380	12.0ª				1
Lu	2.0	0.84798(3)	0.47491(2)	380(10)	16.4ª				1
Y*	*							$Y(Fe_{1-x}Co_x)_{10.8}Re_{1.2}$	4
 Variable composition; see ^a At 4.2 K. Remarks column. ^b At 293 K. 				^c At ^đ In	77 K. μ _B /Fe atom	ı.	° At 13 K.		
References (1) Gueramian et al. (1991) (2) Jurczyk (1990a)				(3) E	Berezyuk et	al. (1994)	(4) Jurczyk (1990b)		

Table 21 Ternary RFe_{12-r}Re₂-type compounds

the presence of other possible magnetic phases which do not contain Fe (Berezyuk et al. 1994). The statement about ferromagnetic coupling of both magnetic sublattices in these compounds is also questioned by inspecting the values of the saturation magnetization listed in table 21. One can see that except for $NdFe_{10}Re_2$ (Gueramian et al. 1991) all

magnetization values are lower, which supports AF coupling with the Fe sublattice for heavier lanthanides.

The Curie points of the compounds with Re are markedly lower than those for compounds with other stabilizing elements, and the location of Re in the 8(i) position seems to cause this behavior (Gueramian et al. 1991). A particularly low value of $T_{\rm C}$ is reported for the nonstoichiometric Pr compound by Berezyuk et al. (1994), who suggested that the pronounced difference between the stoichiometric and nonstoichiometric Pr compounds does not result from the variation in the composition, but is due to the presence of additional magnetic phases without Fe contribution.

3.3.2. Anisotropy

The ThMn₁₂ tetragonal structure (axial) causes anisotropy in the reported compounds. The anisotropy, particularly at low temperature, results predominantly from the lanthanide (R) sublattice; however, as mentioned above it has recently been acknowledged that there is also a substantial contribution from the transition-metal sublattice (Thuy 1994, private communication). The interplay of anisotropy of both sublattices gives the final shape of the total anisotropy and causes the interesting phenomenon of the spin-reorientation transition to be discussed in sect. 3.3.3.

Because of the limited availability of single-crystal materials with the ThMn₁₂-type structure, the anisotropy is frequently evaluated from the examination of field-preoriented samples (see Solzi et al. 1988, Yang et al. 1988a,b) or by the singular-point-detection (SPD) technique of Asti and Rinaldi (1974). As concerns the contribution of stabilizing element M to the total anisotropy, Dirken et al. (1989) claim that this contribution is mostly due to the influence of the lanthanide part, and that this influence is equal for M = Si, V, Mo and W, but significantly smaller in the Ti compounds.

Nevertheless, the total anisotropy of the ThMn₁₂-type compounds result from the contributions of both magnetic-rare-earth and 3d-transition-metal sublattices. The anisotropy of the R sublattice is mostly determined by the crystal-field (CEF) interactions whereas the anisotropy of the transition-metal sublattice is due to anisotropy of exchange interactions. The Hamiltonian for the 4f–3d compounds (see e.g. Stefański and Wrzeciono 1989)is

$$\mathcal{H} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{ex}} = \sum_{m,n} B_n^m O_n^m - g_J \mu_{\text{B}} J \mathcal{H}_{\text{m}},$$

where $B_n^m = \Theta_n \langle r^n \rangle A_n^m$; Θ_n are the Stevens factors (α_J , β_J and γ_J for n=2, 4 and 6, respectively); $\langle r^n \rangle$ are Hartree–Fock radial integrals; A_n^m are CEF potentials; $g_J \mu_B J \mathcal{H}_m$ represents the interaction of the R spin moments with the molecular field \mathcal{H}_m which arises from the 3d neighbours, M, due to interaction between 3d and 4f spins; \mathcal{H}_m is composed of contributions resulting from the R–R and R–M interactions. The former interaction is of the RKKY-type and is comparatively weak and therefore the strength of
\mathcal{H}_{m} is determined predominantly by the R–M interactions, which is represented by the Hamiltonian

$$\mathcal{H}_{\rm m}=2Z_1J_{\rm R-M}(g_{\rm J}-1)\frac{S_{\rm M}}{g_{\rm J}\mu_{\rm B}},$$

where Z_1 is the number of M neighbors of the R atoms and other symbols have the usual meaning. \mathcal{H}_m is parallel to the resultant spin of the 3d sublattice. In first approximation, in the CEF potential only the $B_2^0 O_2^0$ term is considered (Stefański and Wrzeciono 1989). The anisotropy energy is $E_a = E_{\perp} + E_{\parallel}$, where E_{\perp} and E_{\parallel} are ground state energies of the Hamiltonians:

$$\mathcal{H}_{\perp} = B_2^0 O_2^0 - g_{\mathrm{J}} \mu_{\mathrm{B}} \mathcal{H}_{\mathrm{m}} J^x, \qquad \mathcal{H}_{\parallel} = B_2^0 O_2^0 - g_{\mathrm{J}} \mu_{\mathrm{B}} \mathcal{H}_{\mathrm{m}} J^z.$$

 E_a corresponds to the stabilization energy. The exchange field is much stronger than the CEF effect. However, in a more advanced approach (see e.g. Stefański and Kowalczyk 1991) additional CEF parameters B_4^0 , B_6^0 , etc., are involved in a definition of the phenomenological anisotropy constants. In the strong exchange limit valid for the ThMn₁₂-type compounds the anisotropy constants are as follows:

$$\begin{split} K_1 &= -\frac{3}{2}B_2^0 \left\langle O_2^0 \right\rangle - 5B_4^0 \left\langle O_4^0 \right\rangle - \frac{21}{2}B_6^0 \left\langle O_6^0 \right\rangle, \\ K_2 &= \frac{38}{8}B_4^0 \left\langle O_4^0 \right\rangle + \frac{189}{3}B_6^0 \left\langle O_6^0 \right\rangle, \\ K_2' &= \frac{1}{8}B_4^4 \left\langle O_4^0 \right\rangle + \frac{5}{8}B_6^4 \left\langle O_6^0 \right\rangle, \\ K_3 &= -\frac{11}{16}B_6^4 \left\langle O_6^0 \right\rangle. \end{split}$$

The angle between the moment direction and the tetragonal c-axis, assuming both iron and rare-earth sublattices are completely rigid, at 0 K, is given by:

$$\sin^2 \Theta = \left[-K_2 \mp \left(K_2^2 - 3K_1 K_3 \right)^{1/2} \right] 3K_3$$

Therefore, the parameters B_4^4 and B_6^4 are less important because they have no influence on the angle θ . The dependence of free energy $E(\Theta, T)$ was calculated for B_4^0 , and the minimum corresponds to the orientation of the total magnetization vector. It gives also the temperature dependence of the direction of the magnetic moment.

Yan Yu et al. (1994) have tried to overcome the unreasonably large variation in the fitted $B_2^0 O_2^0$ parameter with temperature by taking into account the anisotropy of the R-Fe exchange interactions.

Solzi et al. (1988) have reported that the anisotropy field H_a of YFe₁₁Ti, YFe₁₀Si₂, YFe₁₀V₂ and YCo₁₁Ti exhibits a smooth decrease with temperature. The anisotropy of the Co sublattice (planar for these samples) is smaller than that of the Fe sublattice (axial). In YFe_{12-x}V_x increasing V concentration x decreases the anisotropy field (fig. 40). The same behavior was determined by Pareti et al. (1991) for both Er and Y compounds



Fig. 40. Anisotropy fields H_A versus temperature for various x in YFe_{12-x}V_x alloys (Solzi et al. 1988).



Fig. 41. Calculated anisotropy constant $K = H_A M_s/2$ at $T/T_C = 0.5$ versus V concentration x in RFe_{12-x}V_x alloys, for R=Er (circles), R=Tb (triangles) and R=Y (squares). The Y alloys have $K=K_1$ (Pareti et al. 1991).

(fig. 41), however, the Tb alloys exhibit a maximum for x = 2. Figure 42 (Solzi et al. 1988) shows that substitution of Y by Er decreases the anisotropy, which indicates a negative contribution of Er to the anisotropy of $\text{ErFe}_{10}\text{V}_2$. At the same time a positive contribution of Er to anisotropy is observed in $\text{ErFe}_{11}\text{Ti}$. Andreev et al. (1989) have reported for $\text{RFe}_{12-x}M_x$ (M=V and Ti) the anisotropy field $H_a \approx 1.5$ –2.0 T and strong uniaxial anisotropy of the Fe sublattice comparable to that in the R₂Fe₁₄B-type materials. The highest anisotropy is observed for R = Sm compounds (Andreev et al. 1989), however, the most impressive result has been obtained for the nonstoichiometric compound SmFe₁₀Ti ($H_a = 26.8$ T at 1.5 K, Yang et al. 1988a) but other parameters for this material are less favorable, because the saturation magnetization at the same temperature is $15.6\mu_B/\text{fu}$ and $T_C = 610$ K. Among other lanthanide compounds the anisotropy field determined for



Fig. 42. Anisotropy constant $K = K_1 + 2K_2 + K_3 \pm H_A M_s/2$ versus temperature for YFe₁₀V₂ (open circles) and ErFe₁₀V₂ (closed circles) (Solzi et al. 1988).

GdFe_{10.8}W_{1.2} amounts to 7.0 T at 4.2 K, and for YFe_{10.8}Ti_{1.2} to 5.0 T at 293 K (Verhoef et al. 1988). In turn, YFe₁₀Re₂ demonstrates an increase of H_a from 1.62 T at 4.2 K to 2.5 T at 293 K (Gueramian et al. 1991). Also, Grössinger et al. (1992) discovered a monotonic decrease of anisotropy field with increasing temperature for RFe₁₀V₂ compounds. The anomalies are usually related to the SRT temperature (see sect. 3.3.3), however, for the Ho compound anomalies are detected at lower temperatures (see table 16). For this compound and the compounds of Nd, Sm, Dy, Er and Y the anisotropy field decreases with increasing temperature, while the opposite behavior is expected. This is supposed to result from the fact that the contribution of the fourth-order CEF parameter decreases more significantly with temperature than the second-order contribution for the Tb compound, whereas the opposite trend is observed e.g. for the Dy and Ho compounds. The apparently higher anisotropy of the Sm compounds most probably results from a CEF and exchange-induced admixture of the higher multiplet levels into the ground-state multiplet of Sm³⁺.

In the pseudoternary compounds in which iron is substituted by cobalt one can expect a complicated relation for the anisotropy of both sublattices which in the same crystal structure should exhibit a different character. That is not always true. As can be seen from fig. 38 both $YFe_{10.5}Mo_{1.5}$ and $YCo_{10.5}Mo_{1.5}$ exhibit the same type of anisotropy, favoring an axial magnetic structure (Garcia et al. 1994).

The results of investigations into the domain structure in UFe₁₀Si₂ and UCo₁₀Si₂ (Wysłocki et al. 1990) suggest for both compounds the same axial anisotropy. Again for the rare-earth compounds, e.g. for YFe_{10-x}Co_xV₂, Jurczyk and Chistyakov (1989) have reported a maximum in $T_{\rm C}$ for x=5 but for this composition the anisotropy field is nonmeasurable, and it has been determined only for $x \le 2$ (see fig. 33). Particularly high magnetic anisotropy can be expected for the Sm pseudoternaries and these alloys have been studied further. Andreev et al. (1989) observed that in SmFe_{11-x}Co_xTi $T_{\rm C}$ and $M_{\rm s}$ increase with x whereas the anisotropy of the 3d lattice decreases, i.e., the contribution of the Co sublattice to K_1 is negative. The "optimal" composition

SmFe₈Co₃Ti in terms of M_s exhibits high enough anisotropy field $H_a = 3.2$ MA/m. For the SmFe_{10.8-x}Co_xTi_{1.2} and SmFe_{10-x}Co_xSi₂ systems it has been reported by Solzi et al. (1990) that increasing x produces a rapid decrease of the overall axial anisotropy, leading to a change of sign of the anisotropy, that is, a change to an easy-plane system. This effect is quantitatively different for the two systems reported. Furthermore, comparison with YFe_{10.8-x}Co_xTi_{1.2} alloys indicates that Co has a strong indirect influence on the Sm anisotropy.

To our knowledge no information is available concerning the influence of nickel substitution on sublattice anisotropy. For the uranium compounds $UFe_8Ni_2Si_2$ and $UFe_6Ni_4Si_2$ strongly uniaxial anisotropy is preserved, as indicated in an examination of the domain structure (Wysłocki et al. 1994).

3.3.3. Spin reorientation transition (SRT)

Various figures present the tentative phase diagrams for compounds exhibiting SRT. Note that these are mostly compounds of Fe, nevertheless figs. 32 and 34 show the SRT for $DyCo_{10}V_2$ (Jurczyk et al. 1991b) and fig. 37 that for $Er(Fe, Co)_{10.4}Mo_{1.5}$ (Garcia et al. 1994). In fig. 43 the magnetic phase diagrams of the RFe₁₀Si₂ systems are shown according to Q. Li et al. (1991). Ma et al. (1991) reported T_{SR} for the Dy compound to be 210 K, and Stefański and Kowalczyk (1991) reported $T_{SR} = 48$ K for the Er compound. Both values are slightly different from those presented in fig. 43. Andreev et al. (1993c) point out that there is only one transition in the Tb compound. One should note that for Dy and Tb compounds the anomalies related to SRT are not seen in the thermomagnetic curves measured with a field applied perpendicular to the easy direction. The same authors report $T_{SR} = 120$ K for NdFe₁₀Si₂. Figure 44 shows the RFe₁₁Ti and RFe₁₀V₂ systems



Fig. 43. Tentative phase diagrams for $RFe_{10}Si_2$ compounds (Q. Li et al. 1991).



Fig. 44. Tentative phase diagrams for (left) RFe₁₁Ti and (right) RFe₁₀V₂ compounds (Buschow 1989, J. Hu et al. 1989, Haije et al. 1990).

according to Buschow (1989), J. Hu et al. (1989), Sinha et al. (1989a), Haije et al. (1990) and Andreev et al. (1993a). A recent examination of single crystals of TbFe₁₁Ti and DyFe₁₁Ti by Andreev et al. (1993a) demonstrated that the tentative phase diagram of the first compound is close to that presented by Zhang et al. (1989) (see also fig. 44). They established that T_{SR} is extremely sensitive to the magnetic field in the low-field range (from 250K at 0.3 mT to 325K at 0.15T). As shown in fig. 44, DyFe₁₁Ti is a special case of basal-plane anisotropy. At lower temperature there is a cone, but the cone angle is 80°, which almost corresponds to the basal plane. After a rather special first-order transition from a wide 80° cone to a 45° cone at 120 K, a second-order oneaxis transition occurs at 220 K (Andreev et al. 1990). Christides et al. (1989) determined T_{SR1} and T_{SR2} with low-temperature easy-plane and high-temperature cone structure. H.-S. Li et al. (1988) have claimed that there is an anomaly in the thermomagnetic curve of SmFe₁₁Ti at 150K when a magnetic field of 9T is applied parallel to the c-axis. For $RFe_{10}V_2$ compounds the other authors propose different SRT temperatures than shown in fig. 44, which is most probably due to a different stoichiometry or different magnetic fields used for determining T_{SR} . For TbFe_{10.5}V_{1.5} Pareti et al. (1991) claimed that there are two SRT's, at $T_{SR1} = 198$ K and $T_{SR2} = 211$ K. For the stoichiometric Dy compound also two SRT are reported: $T_{SR1} = 178$ K and 140 K and $T_{SR2} = 220$ K and 215 K by Jurczyk et al. (1991a) and Christides et al. (1989), respectively. The structure of $ErFe_{10}V_2$ is reported to be conical by Moze et al. (1988a), but two SRT's are reported for ErFe_{9.25}V_{2.75}, at 120 and 139 K (Pareti et al. 1991). In fig. 45 the phase diagrams for the $RFe_{10}Cr_2$ systems are shown according to Yang et al. (1991). For these systems different results are reported by Stefański and Kowalczyk (1991) for Er compounds ($T_{SR} = 25$ K).

SRT is usually obtained from $\chi_{ac}(T)$ measurements on polycrystals; however, singlecrystal examinations of HoFe₁₁Ti (Andreev et al. 1993a) and HoFe₁₀Mo₂ (Scherbakova et al. 1993) indicate that the anomaly observed in the $\chi_{ac}(T)$ plot can be connected with other phenomena, e.g. the onset of coercive force and a sharp increase of uniaxial anisotropy with increasing temperature (Scherbakova et al. 1993). ND experiments provide a clear-cut determination of existing magnetic ordering (see Haije et al. 1990).



Fig. 45. Existence range of various magnetic phases in $RFe_{10}Cr_2$ systems (Yang et al. 1991).

The most contradictory situation exists for the Ho compounds, which can be summarized as follows:

- (i) SR is reported for HoFe₁₁Ti (Zhang et al. 1989), HoFe₁₀V₂ and HoFe₁₀Mo₂ (Christides et al. 1989), HoFe₁₀Si₂ (Q. Li et al. 1991), and HoFe₁₀Cr₂ (Yang et al. 1991).
- (ii) there is no spin reorientation in HoFe₁₁Ti (several papers, including the singlecrystal data of Kudrevatykh et al. 1990), HoFe₁₀V₂ (many papers), HoFe₁₀Mo₂ (Ermolenko et al. 1990), and in the single-crystal data of Scherbakova et al. (1993).

Therefore, as mentioned above, the observed anomalies can appear without a change of the anisotropy type, and the interpretation of experiment has to be very careful.

In the majority of known R-3d materials with the axial crystallographic structure, SRT results from the competition of the magnetic anisotropy energy of the R and 3d sublattices. At room temperature the anisotropy of the R sublattice is much weaker than that of the 3d sublattice, but it prevails at cryogenic temperatures. Usually, as mentioned above, the total anisotropy of these compounds is predominantly determined by the firstorder and second-order anisotropy constants ($K_1 = K_{1R} + K_{1d}$, and $K_2 \approx K_{2R}$, because $K_{2d} \approx 0$) which can be expressed in terms of the CEF parameters and the Stevens operator equivalents (see e.g. H.-S. Li and Coey 1991). Even then, if the absolute values of the anisotropy constants are comparable, their different temperature dependencies can cause SRT. The values and signs of the anisotropy constants also determine SRT if in the corresponding compounds an easy axis of magnetization or a plane of easy directions in selected temperature range exist. Complicated equilibria between these factors can create more complicated magnetic structure than with the easy axis or easy plane of magnetization. However, Buschow and de Mooij (1989) deny the existence of conical structure and they claim that this structure can result from the presence of partially magnetically aligned second phase. This statement, although, has not been confirmed.

Another cause of SRT can be competition between the anisotropy constants of the second and higher order in the R sublattice. In the compounds of Nd, Tb and Dy (Andreev et al. 1989) SRT results from the first mechanism ($K_{1R} < 0$, $K_{1d} > 0$ and $K_2 > 0$). However,



Fig. 46. Angle θ between easy axis and *c* versus temperature for (curve 1) DyFe₁₀Mo₂, (curve 2) TbFe₁₀Mo₂ and (curve 3) ErFe₁₀Mo₂ (Ermolenko et al. 1990).

in the light of the first explanation, the absence of SRT in the Ho compounds and the appearance of transition in the $\text{ErFe}_{12-x}M_x$ (M=Ti, V) alloys are both unexpected (Andreev et al. 1989). It has been suggested (Andreev et al. 1989) that the higher-order anisotropy constants have a substantial influence on the behavior of compounds of these two elements because the second-order CEF terms and thus the first-order anisotropy constants are almost meaningless. In these cases the magnetic field has a strong influence on the location of SRT.

As can be seen from fig. 46 for RFe₁₀Mo₂ (R = Dy, Tb and Er) (Ermolenko et al. 1990) and from fig. 47 for DyFe₁₁Ti (B.-P. Hu et al. 1989b), the tilting angle can be a smooth function of temperature. But this dependence can be irregular, as is presented in fig. 47 for TbFe₁₁Ti (B.-P. Hu et al. 1989b) and also for TbFe₁₀Cr₂ and DyFe₁₀Cr₂ (Stefański 1990). Christides et al. (1989) proposed a simple model to estimate the tilting angle α between the magnetization direction and the tetragonal *c*-axis. This model assumes a distribution of the *c*-axis around the oriented direction. Using the distribution function $P(\theta) = [(n + 1)2\pi] \cos^n \theta$, one finds:

$$\frac{\langle M_{\parallel} \rangle}{M_{\rm s}} = \frac{n+1}{n+2} [\cos \alpha + c(n) \sin \alpha],$$
$$\frac{\langle M_{\perp} \rangle}{M_{\rm s}} = \frac{n+1}{n+2} c(n) \cos \alpha,$$
$$\frac{\langle M_{\parallel} \rangle}{\langle M_{\perp} \rangle} = c(n)^{-1} + \tan \alpha,$$



Fig. 47. Canting angle θ between the magnetization direction and the *c*-axis for RFe₁₁Ti (triangles, R=Dy; circles, R=Tb) versus temperature (B.-P. Hu et al. 1989b). The solid lines correspond to the calculated values (J. Hu et al. 1988). The experimental results are deduced from the ⁵⁷Fe Mössbauer spectra. Similar results were obtained for TbFe₁₀Cr₂ and DyFe₁₀Cr₂ by Stefański (1990).

Fig. 48. Spin-reorientation temperature $T_{\rm SR}$ determined by ac susceptibility (circles) and calculated with CEF parameters of B.-P. Hu et al. (1990) (dashed curve) and with readjusted parameters (Nagamine and Rechenberg 1992) (solid curve) versus Gd concentration x in $Dy_{1-x}Gd_xFe_{11}Ti$ alloys. One can see that for higher Gd content ($x \ge 0.8$) $T_{\rm SR}$ falls below 80 K.

where the constant $c(n)^{-1} = (\pi/2)n!!/(n-1)!!$ (*n* is an odd number, and is equal to the ratio $\langle M_{\parallel} \rangle / \langle M_{\perp} \rangle$ when α vanishes. The calculated temperature dependence of the tilting angle is demonstrated in fig. 47 (B.-P. Hu et al. 1989b). The SRT temperature can be precisely determined, although the values of α (= θ in fig. 47) may not be entirely reliable.

The temperature of the SRT can be influenced by a change of composition. Figure 30 (H. Yang et al. 1993) shows that the SRT decreases monotonically with increasing V content in $NdFe_{12-x}V_x$. In the case of $Dy_{1-x}Gd_xFe_{11}Ti$ alloys, the SRT temperature as shown in fig. 48 decreases with increasing Gd concentration x; Gd in this case plays the role of a diluter (Nagamine and Rechenberg 1992). One can see that the experimental points are in fair agreement with calculation in terms of the CEF parameters (B.-P. Hu et al. 1990) and in terms of the readjusted parameter (Nagamine and Rechenberg 1992). The role of a dilutent is also attributed to Y, and the decrease of the neodymium sublattice anisotropy in (Nd, Y)Fe₁₁Ti with an admixture of Y is believed to be a cause

of the observed reduction of the SRT (Luong et al. 1990). The results of admixture of Co instead of Fe are presented for Nd(Fe, Co)_{10.2}Mo_{1.8} (fig. 36, Luis et al. 1994), TbFe_{10.8-x}Co_xW_{1,2} (fig. 39, Jurczyk and Rao 1991), DyFe_{10-x}Co_xV₂ (fig. 34, Jurczyk et al. 1991a), ErFe_{10.5-x}Co_xMo_{1.5} (fig. 37, Garcia et al. 1994) and YFe_{10.5-x}Co_xMo_{1.5} (fig. 38, Garcia et al. 1994). The magnetic phase diagram T(x, M) for TbFe_{10.8-x}Co_xW_{1.2} alloys (Jurczyk and Rao 1991) is relatively simple, but the alloys exist in a limited concentration region up to $x \lesssim 5$. Also, the magnetic phase diagram of YFe_{10.5-x}Co_xMo_{1.5} exhibits only two magnetic phases. The conical structure exists over a limited composition and temperature range and is supposed to result from competition of different anisotropy types in the Fe and Co sublattices. Further, NdCo_{10.2}Mo_{1.8} (fig. 36, Luis et al. 1994) exhibits an axial structure similar to that of the ternaries at higher temperature (at which the Nd sublattice does not contribute to total anisotropy). $ErFe_{10.5}Mo_{1.5}$ and $ErCo_{10.5}Mo_{1.5}$ also demonstrate axial anisotropy at higher temperature (fig. 37, Garcia et al. 1994). This unexpected behavior of the compounds with Mo as the stabilizing element can result from location of Mo in the 8(i) positions which significantly diminish the magnetic importance of the transition-metal sublattice and in turn its contribution to the total anisotropy. This conclusion is confirmed by substantially lower Curie points of above mentioned systems in relation to those with other stabilizing elements.

Arnold et al. (1993) have discussed the influence of pressure on the SRT. They propose that the second-order CEF terms are mainly sensitive to the pressure and that the applied pressure only slightly influences the fourth- and sixth-order CEF terms and the intensity of the R-Fe exchange interactions. The results for $RFe_{10}V_2$ (R=Nd, Dy and Er) under hydrostatic pressure up to 10 Kbar show no evidence of any change of the SRT temperature in the range of applied pressure, which confirms the negligible influence of the external pressure on higher-order terms.

3.3.4. Theoretical considerations

The theoretical discussions applied to the explanation of magnetic behavior of the Th Mn_{12} -type compounds can be easily divided into two groups. The first group is based on the combination of the CEF (in point-charge approximation) and molecular-field approximation (MFA) models and has had considerable success in consideration of the anisotropy, spin-reorientation transitions, and the temperature and field dependences of the magnetic parameters.

The second group comprises calculations of the band structures and related properties. This also includes the so-called "magnetic valence model", which is a modification of the band approach.

Below, we describe mainly the band-structure calculations, because the first approach has already been discussed in the sections devoted to anisotropy and SRT; for that group we now present some additional information which we had previously omitted.

Stefański and Kowalczyk (1991) used a more developed formula for the exchange Hamiltonian:

$$\mathcal{H}_{\rm ex} = 2g_{\rm J}\mu_{\rm B}\mathcal{H}_{\rm m}(J^z\cos\theta + J^x\sin\theta),$$

where θ represents the angle between the *c*-axis and the magnetic moment direction, and \mathcal{H}_m is the molecular field arising from the transition-metal sublattice. The value of \mathcal{H}_m has been evaluated, e.g., for ErFe₁₀Cr₂ by Stefański et al. (1989b) in the mean-field approximation: $\mathcal{H}_m = 12[T - (81 \text{ K}/\mu_B)]$. The temperature dependence of the molecular field approximated by Gubbens et al. (1985) is:

$$\mathcal{H}_{\mathrm{m}}(T) = \mathcal{H}_{\mathrm{m}}(0) \left[1 - 0.5 \left(\frac{T}{T_{\mathrm{C}}} \right)^2 \right].$$

A charge of 3+ for the rare-earth ion and 0 for transition metals and stabilizing elements were assumed by Stefański and Kowalczyk (1991) and they performed summations over the nearest neighbors (nn) and next-nearest neighbors (nnn) to establish a sum and magnitude of the CEF parameters and the intersublattice molecular field \mathcal{H}_m , acting on the R ion and resulting from, e.g., surrounding Fe atoms (R–R exchange interactions are considerably smaller according to Stefański et al. 1989b). \mathcal{H}_m can be expressed as:

$$\mathcal{H}_{\rm m} = 2(g_{\rm J}-1)\frac{\mathcal{H}_{\rm ex}}{g_{\rm J}}, \quad \mathcal{H}_{\rm ex} = \frac{J_{\rm RFe}Z_{\rm I}S_{\rm Fe}}{\mu_{\rm B}},$$

with z_1 the number of Fe nn of the R atom, and J_{RFe} a coupling parameter describing interactions between R and Fe sublattices. To estimate this parameter the MFA is applied and

$$T_{\rm C} = 3k_{\rm B}T = a_{\rm FeFe} + (a_{\rm FeFe}^2 + 4a_{\rm FeR}a_{\rm RFe})^{1/2};$$

neglecting weak R-R interactions we get

$$a_{\text{FeFe}} = zJ_{\text{FeFe}}S_{\text{Fe}}(S_{\text{Fe}}+1)$$

and

$$a_{\rm FeR} a_{\rm RFe} = z_1 z_2 S_{\rm Fe} (S_{\rm Fe} + 1) (g_{\rm J} - 1)^2 J (J + 1) J_{\rm RFe}^2$$

where z_2 is the number of next-nearest neighbors.

Stefański and Kowalczyk (1991) obtained the free energy by diagonalizing the Hamiltonian $\mathcal{H} = \mathcal{H}_{CEF} + \mathcal{H}_{ex}$ within the ground-state manifold and then calculating the partition function $Z(\theta, T)$. The free energy of the rare-earth ion is $E_R(\theta, T) = -kT \ln[Z(\theta, T)]$. The total free energy must also include the non-negligible contribution of the transition-metal sublattice E_T which is approximated by $E_T = K_{1T}(T) \sin^2 \theta$, where K_{1T} is the secondorder anisotropy constant. Usually in this approach the dependence of the free energy on the CEF parameters near 0 K is presented. Christides et al. (1991a) observed a decrease of $B_n^m \langle O_n^m \rangle$ CEF parameters with increasing stabilizing element atom occupation of the 8(i) site. R.-W. Huang et al. (1993) have anticipated the temperature dependence of



Fig. 49. Spin-polarized densities of states (DOS) for $YFe_{10}V_2$ calculated in terms of the linear-muffin-tin-orbitals (LMTO) model. The zero on the energy scale corresponds to the Fermi energy (Jaswal et al. 1990).

magnetization using the two-sublattice molecular-field theory. The results for $RFe_{10}V_2$ are consistent with the experimental data.

We will now discuss the results of band calculations. Jaswal et al. (1990) have carried out band-structure calculations for $YFe_{10}V_2$ and $YFe_{10}Cr_2$. These compounds were chosen because they permit the study of the main features of the electronic structure of these systems without the theoretical complications resulting from the lanthanide 4f electrons. The self-consistent spin-polarized electronic structure calculations are based on the linearmuffin-tin-orbitals (LMTO) method in the semirelativistic approximation. The core states for the constituent atoms are frozen to be the same as the atomic sites found selfconsistently. The s, p and d basis functions were used for the valence states of each atom. The calculated spin-polarized densities of states (DOS) for both compounds are quite similar as seen from figs. 49 and 50, respectively, with the main peaks being due to Fe d states and the contributions due to V and Cr being relatively small. The results of the calculations are compared with the photoemission data presented in fig. 51 and 52. Note that the experimental data are taken below and above the Curie temperature of both compounds. The paramagnetic electronic structure is essentially unchanged from that of the ferromagnetic phase in both systems. The O2 and/or C contamination peak observed at -6 eV in the low-temperature (293 K) curve for the Cr compound (fig. 52) nearly vanishes at high temperature due to thermal desorption. The similarity of the



Fig. 50. Spin-polarized densities of states (DOS) for $YFe_{10}Cr_2$ calculated in terms of the linear-muffin-tin-orbitals (LMTO) model. The zero on the energy scale corresponds to the Fermi energy (Jaswal et al. 1990).

paramagnetic to ferromagnetic spectrum in iron is well known and it is due to the shortrange magnetic order. All these figures show that the calculated DOS's are in good overall agreement with the experimental data. The calculated magnetic moments per formula unit are 16.8 and $17.2\mu_B$ for YFe₁₀V₂ and YFe₁₀Cr₂, respectively. They are in good agreement with experimental values (see e.g. de Boer et al. 1987, Helmholdt et al. 1988a). The calculations give sizeable moments at Y and V (Cr) sites which couple AF to the Fe moments. CEF parameters have also been calculated, and comparison of these with experimental values clearly confirm the inadequacy of the point-charge model (PCM) in CEF calculations.

In additional self-consistent spin-polarized calculations to determine the DOS, charge transfer and magnetic properties Jaswal (1991) has shown that the simplified tightbinding calculations lead to an unexpectedly large moment for the stabilizing atom (~1 μ_B) coupled AF with the Fe atoms. The V atoms prefer to substitute for Fe on the 8(i) sites in the Fe compound and the same preference is assumed to hold in YCo₁₀V₂. The main contribution to DOS comes from Co, primarily due to Co 3d states. The average exchange splitting is about 1 eV for Co d states. The calculated magnetization per formula unit is 9.11 μ_B and 8.11 μ_B for Co atoms located in two crystallographic positions: A ($\pm \alpha 00$) and B ($\alpha 00$, $0 \alpha 0$), respectively. The experimental value of 7.16 μ_B for the B configuration was found by Jurczyk (1990c). The charge transfers for YCo₁₀V₂ are quite small.



Fig. 51. Photoemission data taken above (618 K) and below (293 K) the Curie point in relation to the broadened total density of states (DOS) of $YFe_{10}V_2$. The zero on the energy scale corresponds to the Fermi energy (Jaswal et al. 1990).

Fig. 52. Photoemission data taken above (603 K) and below (293 K) the Curie point in relation to the broadened total density of states (DOS) of $YFe_{10}Cr_2$ (multiplied by a zero-temperature function). The zero on the energy scale corresponds to the Fermi energy (Jaswal et al. 1990).

Self-consistent *ab initio* band-structure calculations using the augmented-sphericalwave method have been carried out by Coehoorn (1990) for hypothetical YFe₁₂ and YFe_{12-x} M_x (M=Ti, V, Cr, Mo, and W). The calculated value of magnetic moment per Fe atom is $2.02\mu_B$, in good agreement with experiment, particularly if one takes into account that the experimental total moment also contains a small orbital contribution,

estimated to be ~0.05–0.10 μ_B per Fe site in YFe₁₂. At present it is difficult to decide whether the relatively large contribution of the R atoms to the total magnetization and the magnetocrystalline anisotropy when the stabilizing atom prefers to occupy an 8(i) site is of greater importance than the disadvantage associated with the relatively large reduction in moment. The decrease in magnetic moment due to substitution of the magnetic atom by the stabilizing atom is found in the above calculations to be insensitive to the type of stabilizing atom, contrary to experiment. Therefore, these calculations seem to be unsuccessful.

For another hypothetical binary compound, $GdFe_{12}$, electronic structure calculations by means of the LMTO-ASA method have been carried out by Trygg et al. (1992), as mentioned in sect. 3.1.2 on the magnetic properties of the binaries with Fe. The R-4f magnetic moments were obtained from the standard Russell-Saunders scheme but the radial 4f spin density was otherwise part of the self-consistent band calculation. The influence of localized 4f magnetism on the conduction-band magnetism is found to produce little or unnoticeable changes in the local moment of the iron. The total magnetic moment is calculated to be $24.61\mu_B/fu$ when the 4f is included and $24.62\mu_B$ when the 4f moment is set equal to zero.

Also, some calculations concerning the ternaries $YFe_{11}Ti$ and $YFe_{11}TiN$ have been reported. Sakuma (1992) has performed spin-polarized band calculations with the LMTO– ASA method in the frame of local-spin-density functional formalism. Analysis of asphericity parameters predicts that the N atoms attract the wave function of the Y atoms rather than that of the Fe atoms and in turn release the Fe atoms from bonding with Y atoms. By this effect, the magnetic moment of Fe increases, besides expanding the lattice. The magnetic moments of the nn Fe atoms of the N site are lowered with inclusion of N atoms while the Fe atoms furthest from N have the largest moment. The spin fluctuation theory developed by Mohn and Wohlfarth is shown to give a fair description of the change of the Curie point due to nitrogen absorption.

Electronic total energy calculations (Sakuma 1993) for YFe₁₁Ti, performed in terms of the same model, predict that the system is most stable when the Ti atoms are located at the 8(f) sites, while experimental results suggest that they are at the 8(i) sites. On the other hand, the calculated equilibrium volume of the unit cell exhibits fair agreement with the measured value. It is also shown that the unit cell volume increases with Ti concentration x in YFe_{12-x}Ti_x, with a rate $\Delta V / \Delta x = 10 \text{ Å}^3 / \text{unit cell}$, and the magnetic moment decreases with a rate $\Delta M/\Delta x = -4\mu_{\rm B}$ consistent with the calculations of Coehoorn (1990). A direct comparison with experimental values for the $YFe_{12-x}Ti_x$ system is impossible because results for M are known for x = 1.0 and 1.2 only. However, the value of $\Delta M/\Delta x \approx -4\mu_{\rm B}$ is obtained from the experimental determination of magnetization of $YFe_{12-x}V_x$ alloys (Verhoef et al. 1988). The same quantity obtained from Mössbauer effect examination amounts to $3.3\mu_{\rm B}$ (Denissen et al. 1990) if one applies a conversion factor of 14.5 T/ μ_B (Gubbens et al. 1988). The total magnetic moment of YFe₁₁Ti (x = 1) is calculated to be about $21.7\mu_{\rm B}$ (Sakuma 1993). With inclusion of the spin-orbit interaction in the LMTO Hamiltonian, the orbital magnetism and the magnetocrystalline anisotropy were further evaluated. The orbital magnetic moment per Fe atom is about $0.06\mu_{\rm B}$ and the

anisotropy energy is obtained as $97 \mu Ry/fu$. This value leads to about 12.1×10^6 erg/cc. Although the value is quite large for a Fe compound, it is still about the half of the measured value, 23×10^6 erg/cc.

In turn, self-consistent spin-polarized electronic structure calculations using the linearmuffin-tin orbitals have been performed by Fernando et al. (1993) for NdFe₁₁Ti, $NdCo_{10}V_2$ and $YCo_{10}Si_2$, and by Jaswal (1993) for $NdFe_{11}TiN_x$. The calculated density of states near the Fermi edge in the Fe compounds is dominated by the Fe 3d states and for the nitrogenated compounds the N(2p) peak is evident around 6.3 eV. In these last compounds there is no visible shift in Fe 3d peaks. Apart from small energy shifts in the peak positions, there is an overall agreement between the experimental data (XPS) and the calculated DOS. The calculated magnetization does not change much upon nitrogenation in NdFe₁₁TiN_x, but the calculated value is larger than the experimental results obtained in ⁵⁷Fe Mössbauer-effect and neutron-diffraction (ND) experiments. Similarly as Sakuma's (1992) results, the increase in the Curie temperature on nitrogenation, calculated on the basis of SF theory (Jaswal 1993), is in good agreement with the experimental results. The single-ion anisotropy of Nd, based on its valenceelectron distribution, changes from a planar to a c-axis configuration upon nitrogenation, in qualitative agreement with the experimental results. Generally, it seems that the magnetic Nd sublattice does not substantially influence the results of calculations and experiment in relation to the La, Lu and Y compounds.

The experimental photoemission spectra for $NdCo_{10}Cr_2$ and $YCo_{10}V_2$ are quite similar because they are dominated by the Co 3d states at this photon energy just like the spectra of the Fe compounds. The principal peak at the Fermi edge due to the Co 3d states agrees with the calculated DOS. The second Co 3d peak, near 2.3 eV, is not noticeable in the experimental spectra due to a considerable broadening, resulting from many-body effects in Co, which are not included in the calculated DOS. After some modifications, a good agreement is obtained between photoelectron energy distribution curve and calculated DOS (Fernando et al. 1993).

Ishida et al. (1994) have calculated the dependence of the magnetic properties on Mo concentration and the type of Mo sites in the YFe_{12-x}Mo_x system. For the calculations of the energy eigenvalues they used the LMTO–ASA method in the nonrelativistic approximation, and the exchange-correlation potential within the framework of the LSD approximation. The densities of states (DOS) were calculated by the tetrahedral integration method of Rath and Freeman (1975). Ishida et al. (1994) have computed the magnetic moment and total energy of YFe₁₁Mo, YFe₉Mo₃ and YFe₈Mo₄ versus lattice parameter *a* for the Mo atoms occupying 8(f), 8(i) and 8(j) sites. They found that the total energy is lowest for the case where the Mo atoms occupy 8(f) sites. As mentioned above, Sakuma (1993) found the same preference for the Ti atoms in YFe₁₁Ti, but these results are in conflict with the experimental findings which show at most a preference for transition metal to occupy the 8(i) positions (see e.g. Sun et al. 1993a, Yellon and Hadjipanayis 1992). Sun et al. (1993b) reported, however, that Mo atoms were located at both the 8(i) and 8(f) sites. The lattice parameter was determined so as to minimize the total energy, but the difference between the Mo sites is small and this could be at the

origin of the results reported by Sun et al. (1993b). The DOS was calculated considering the Mo atoms located in the 8(f) and 8(i) sites. The local DOS of the Fe (8f), Fe (8i) and Fe (8j) atoms are similar to those of YFe_{12} which were calculated by Asano et al. (1993), but are different in detail. It is found that the Mo d states hybridize well with the valence states of the surrounding atoms. The occupation number of the down-spin states is more than any of the up-spin states so that the magnetic moment on the Mo atoms amounts to $0.3-0.6\mu_B$ and is parallel to those on the Fe atoms. The hybridization between the Mo and Fe valence states produces changes in the DOS of the Fe d states from those for YFe_{12} . As concerns the magnetic moment, regardless of the Mo concentration in $YFe_{12-x}Mo_x$, the moment at the Fe sites becomes larger for Fe (8f), Fe (8j) and Fe (8i) sites in that order. There is a general tendency for the moment at each Fe site to decrease with increasing Mo concentration. The decrease comes mainly from the hybridization between the Mo d states and the d states of the Fe atoms which are near the Mo atoms. The experimental values decrease more rapidly than the calculated ones.

Christides et al. (1991b) have applied a simplified method for the interpretation of the experimental data for Y(Fe, Co)_{12-x}T_x compounds by extending the magnetic valence model (MVM) on the Friedel picture of the DOS. The MVM (see Williams et al. 1983, Malozemoff et al. 1984) basically amounts to counting electrons in a rigid band scheme while ignoring the nature of the crystal structure. In spite of this simplification the MVM has been quite successful in characterizing the behavior of the magnetic moments in strongly ferromagnetic systems. Writing the Y(Fe, V)₁₂ compounds in the form $Y_{1-b-c}Fe_bV_c$, the average magnetic moment predicted by the MVM for this formula unit is:

$$\langle M \rangle = b[2N_{3d}^{\uparrow} - Z_{Fe}] - cZ_V - (1 - b - c)Z_Y + 2N_{sp}^{\uparrow} = \langle Z_m \rangle + 2N_{sp}^{\uparrow}$$

Here: (i) N_{3d}^{\uparrow} is the number of 3d electrons in the Fe spin-up band, (ii) Z_i is the chemical valence of atom *i*, (iii) N_{sp}^{\uparrow} is the number of electrons in the unpolarized s-p conduction bands and (iv) $\langle Z_m \rangle$ is the average magnetic valence of the compounds, which for the pseudoternaries considered by Christides et al. (1991b) has the form

$$\langle Z\rangle=\sum x_i Z_{\mathbf{m}_i},$$

and x_i are the relative concentrations of the constituent atoms. Since this model assumes, as mentioned, strong ferromagnetism, there are only spin-down 3d electrons at the Fermi level. Thus we take $N_{3d}^{\dagger} = 5$. The chemical valencies for Fe, Y and V are 8, 3 and 5, respectively. Band calculations show that $N_{sp}^{\dagger} = 0.3$ for the late transition metals while addition of early transition metals or non-transition elements increases N_{sp}^{\dagger} to 0.45 (Malozemoff et al. 1983). A modification of the MVM introduced by Christides et al. (1991b) considers the solute transition element T as scattering centers embedded in Fe positions which produce resonance states above the Fermi level. The broadening of these levels due to s–d admixture effects, leads to a part of the impurity d state which lies

below the host Fermi energy and affects the d-band magnetism. As mentioned above the unmodified MVM can be applied for strong ferromagnetism. To improve the model it is necessary to obtain a quantitative estimate of N_d for the solute transition metal. The effect of the perturbing potential localized at the vicinity of a transition-metal impurity in Fe, Co or Ni is to create localized, virtual bound d states which, depending on their relative position with respect to the Fermi level, may or may not be occupied. Furthermore, the sd admixture effect will cause a broadening in energy of the relatively localized impurity states, which spreads out over an energy range γ . The impurity can be considered as a scattering center for "free" electrons in the host sp band and d band (at least those electrons near the bottom of the d band), providing the impurity concentration is low, i.e., solute atoms can be described as isolated impurities acting as scattering centers and producing d-resonance states around an energy E_d . When the Fermi energy E_F is well above E_d the resonance states are completely occupied; they are empty when E_F is much less than E_d . For the intermediate solution, where E_d is close to E_F , Harrison (1980) has proposed the following relation for the fractional occupation for spin-up, n^+ , and spindown, n^- , states of impurity atoms:

$$\tan(\pi n^{\pm}/5) = \frac{\Gamma}{2(E_{\rm d}^0 + n^{\mp}U_{\rm x} - E_{\rm F})},$$

where Γ is the resonance width, E_d^0 is the energy of the resonance without exchange, and U_x is the exchange interaction for each pair of d electrons of the same spin on the same atom. One cannot expect that, in Y(Fe, Co)_{12-x}V_x, the Y and V atoms carry a magnetic moment. Solving the above equation for the case $n_d = n^+ = n^-$, where N_d appears in the equation

$$Z_{\rm m}=2N_{\rm d}-Z,$$

with Z_m the magnetic valence, Z the number of valence electrons and N_d the number of d electrons of the majority spin band, one gets $N_d = 5n_d$. The energy of the resonance without exchange, E_d^0 , is determined with respect to the bottom of the sp band of the host. The position of the bottom of the sp band of V against the free continuum states is determined by the relation

$$E_{\rm sp} = \varepsilon_{\rm d} + 8V_{\rm ss},$$

where ε_d is the Hartree-Fock energy of the atomic d state and V_{ss} is an appropriate matrix element given by $V_{ss} = -1.4h^2/2\pi md^2$ (Harrison 1980) in which d is the average distance of the nearest neighbors calculated from the atomic volume of the element and $h^2/2\pi m = 7.62 \text{ eV} \text{ Å}^2$. Using the computed values of E_{sp} , the position of the impurity d band in the energy-level scheme of the host is given by

$$E_{\rm d}^{\rm 0}({\rm V}) = [E_{\rm sp}({\rm Co}) - E_{\rm sp}({\rm V})] + E_{\rm d}({\rm V}),$$

where $E_d(V)$ is the energy at the middle of the 3d band of the V metal. The exchange energy U_x is also computed from atomic parameters. The value of Γ can be determined from the relation

$$\Gamma = \frac{2W_{\rm d}}{n_l'(x)/j_l'(x) - n_l(x)/j_l(x)} \quad (l = 2),$$

where $j_l(x)$ and $n_l(x)$ are, respectively, Bessel and Neumann functions with argument $x = K_d r_0$, and W_d is the bandwidth. The parameters K_d , r_0 and W_d have been tabulated by Harrison (1980). It is to be noted that the bandwidth W_d used in this calculation corresponds to the solute metal assuming that the local DOS around the impurity is adjusted to come closer to the DOS of the solute. Using these parameters and Fermi energies $E_F(Fe) = 8.8 \text{ eV}, E_F(Co) = 12.49 \text{ eV}$ and $E_F(Ni) = 12.13 \text{ eV}$ given by bandstructure calculation, Christides et al. (1991b) have calculated the values $2N_d$ and the corresponding magnetic valence for transition metals of the first, second and third rows of the Periodic Table. N_d depends on the electronic character of the solute due to different values of E_d , which differs for the elements in a column of the Periodic Table and results in non-integer values of Z_m in contrast to the simple model. This is a considerable improvement in the interpretation of experimental results in relation to the simple model; however, the agreement with experiment is strongly dependent of the assumption of strong ferromagnetism in the band structure of the host metal.

One can see from the above discussion that the theoretical understanding of the $ThMn_{12}$ -type compounds is still very superficial yet. We hope that the present review will be a challenge for fellow theoreticians by supplying them with vast amount of experimental facts.

3.3.5. Improvement of magnetic parameters

Improvement of magnetic parameters can be achieved in two ways: (a) admixture of other components with preservation of crystal structure, and (b) technological processes. Usually, application of each of these two ways results in obtaining samples with a complex stoichiometry, and not necessarily single phases with α -Fe as impurity or other neighbor phases.

3.3.5.1. Admixture. Admixture of Co to Fe alloys, or alloying with other rare-earth elements, was discussed in sect. 3.3.1 dealing with magnetic properties of the ternaries or pseudoternaries with high concentration of Fe, Co and Ni. The interstitials with N and H as mentioned in the introduction are not discussed here because these materials have already been dealt with in a number of review and extended papers (see e.g. Coey 1991, Coey et al. 1991, Liao et al. 1991, Yang et al. 1991a,b, Coey and Hurley 1992, Gong and Hadjipanayis 1992, Hurley and Coey 1992, Wallace and Huang 1992, Tomey et al. 1993). However, the carbon admixture does not enter interstitial sites but occupies 8(i) sites. The magnetic data are shown in table 22. In contrast to the nitrides the substitution of carbon atoms does not change the Curie temperature for $RTiFe_{10.25}C_{0.25}$ (Y.-C. Yang et al. 1993) but a higher amount of carbon has the same influence as nitrogen.

			··· ·			JE	
R	x	a (nm)	с (nm)	<i>Т</i> с (К)	$M_{ m S}$ ($\mu_{ m B}/{ m fu}$)	Remarks	Ref.
RFe ₁	1TiC _{1-x}						
Y	<0.2	0.858	0.481	678	20.5 ^a 15.5 ^b	axial, $\Delta V/V = 2.1\%$, $\Delta T_C/T_C = 29.4\%$	1
	0.1	0.858	0.4798	678	21.6ª	axial, $\Delta V/V = 1.73\%$	2
	0.75	0.8491	0.4797	539	19.01 ^c 2.0 ^d 1.76 ^{d,b}	axial, $\Delta V/V = -0.2\%$	3
Nd	0.1	0.862	0.482	670	20.7 ª 20.2 ^b	axial, $\Delta V/V = 2.0\%$, $\Delta T_{\rm C}/T_{\rm C} = 22.5\%$	1
Sm	<0.2	0.858	0.480	698	18.0ª	planar ^e , $\Delta V/V = 0.9\%$, $\Delta T_{\rm C}/T_{\rm C} = 19.5\%$	1
	0.75	0.8544	0.4791	595	19.52ª	axial, $\Delta V/V = -0.4\%$	4,5
Gd	<0.2	0.858	0.481	734	14.9ª 13.3 ^b	axial, $\Delta V/V = 1.2\%$, $\Delta T_{\rm C}/T_{\rm C} = 20.9\%$	1
	0.75	0.8537	0.4790	620	12.88°	axial, $\Delta V/V = -0.4\%$	1
Тb	<0.2	0.857	0.481	714	11.6ª 12.1 ^b	axial, $\Delta V/V = 1.7\%$, $\Delta T_{\rm C}/T_{\rm C} = 29.3\%$	1
	0.75	0.8528	0.4788	572	10.47°	planar at RT = -0.6% , $T_{\rm SR} > \rm RT$	3
Dy	<0.2	0.857	0.479	697	9.6° 10.1 ^b	axial, $\Delta V/V = 2.3\%$, $\Delta T_C/T_C = 30.5\%$	1
	0.75	0.8510	0.4785	548	9.83°	axial, $\Delta V/V = -0.5\%$, $T_{\rm SR} = 220$ K	3
Ho	<0.2	0.855	0.479	691	8.4ª,ſ 9.4 ^{b,ſ}	axial, $\Delta V/V = 1.4\%$, $\Delta T_{\rm C}/T_{\rm C} = 32.9\%$	1
	0.75	0.8498	0.4784	534	9.99°	axial, $\Delta V/V = -0.5\%$, $T_{\rm SR} = 40$ K	3
Er	<0.2	0.856	0.479	685	11.1 ^{a,f} 13.1 ^{b,f}	axial, $\Delta V/V = 2.0\%$, $\Delta T_C/T_C = 35.6\%$	1
	0.75	0.8487	0.4782	526	10.29°	axial, $\Delta V/V = -0.5\%$	3
Tm	<0.2	0.855	0.478	686	16.1 ª 18.9 ^b	axial, $\Delta V/V = 1.7\%$, $\Delta T_{\rm C}/T_{\rm C} = 38.3\%$	1
Lu	<0.2	0.855	0.478	682	17.1 ª 16.0 ^b	axial, $\Delta V/V = 2.0\%$, $\Delta T_{\rm C}/T_{\rm C} = 39.7\%$	1
RFe ₁	SiC,						
Ce	0.5	1.0049(4) ^g	0.6528(3) ^g	390	13.2ª 6.5 ^h	$M_{\rm s} = 1.32^{\rm d}$	6 6
Pr	0.5	1.0107(3) ^g	0.6534(2) ^g	430	17.1 ^a 9.2 ^h	$M_{\rm s} = 1.39^{\rm d,c}$	6 6
Nd	0.5	1.0083(3) ^g	0.6529(2) ^g	410	17.55° 8.4 ^h	s.c., $M_s = 1.42^{dc}$ Additions ^e	6 6
Sm	0.5	1.0092(7) ^g	0.6538(4) ^g	460	14.8ª	$M_{\rm s}=1.41^{\rm dc}$	4 6

Table 22 Ternary carbides and carbosilicides of various types

continued on next page

Table 22, continued										
R	x	a (nm)	с (nm)	<i>Т</i> с (К)	$M_{ m S}$ ($\mu_{ m B}/{ m fu}$)	Remarks	Ref.			
R(Fe,	Me) ₁₂ C									
Sm*						Sm(Fe, Al) ₁₂ C ^e	4,5			
						Sm(Fe, Ga) ₁₂ C ^c	4,5			
						Sm(Fe, V) ₁₂ C ^e	4,5			
						$Sm(Fe, Cu)_{12}C^{e}$	4,5			
* Var ^a At 4	iable com 4 2 K	position; see	Remarks colu	ımn.	° Sm order	all amounts of C added (also	B, Si and Al) in			
^b At 290 K.					^f No difference with $RFe_{11}Ti$ compounds.					
° At 1.5 K.					^g BaCd ₁₁ -type phase.					
^d In $\mu_{\rm B}$ /Fe atom.					^h At 300 K.					
Refer	ences									
(1) Hurley and Coey (1992)					(4) Singleton et al. (1988)					
(2) QN. Qi et al. (1992)					(5) Strzeszewski et al. (1989)					
(3) YC. Yang et al. (1993)					(6) Le Roy et al. (1987)					

Y.-C. Yang et al. (1993) claim that carbon substitution increases both saturation magnetization and magnetocrystalline anisotropy. This conclusion is confirmed by other authors (see table 22). One can see that the silicide carbides of light rare earths exist with a different crystal structure of the BaCd₁₁-type (I4₁/amd space group) in which the carbon atoms fill octahedral vacancies formed by four iron and two lanthanide atoms, with an occupancy of 25%. These compounds exhibit Curie temperatures which are lower than for corresponding the ThMn₁₂-type phases; they lie between 390 and 460 K. The mean iron moment amounts to about $1.4\mu_{\rm B}$ at low temperature (Le Roy et al. 1987).

Anagnostou and Niarchos (1990) reported on structure and magnetic properties of meltspun SmFe_{10.8}Ti_{1.2}B_x alloys with x = 0.2 and 0.4. The added boron acts as a glass former and leads to amorphous ribbons, but after annealing a partial crystallization to the ThMn₁₂ phase is observed. A best coercivity of about 0.6 T was obtained in ribbons annealed at 850°C for 5 min.

The coercivity of melt-spun NdFe₁₀Cr₂-Nd_{0.67}B_{0.33} alloys was investigated by S.H. Huang et al. (1990). However, the alloys were multiphase mixtures with presence of Nd₂Fe₁₄B phase and coercivity amounting to 0.85 kOe.

The magnetic data for Sm-Fe-Ti derivatives, which were obtained as ribbons annealed at 800°C by Wang and Hadjipanayis (1990), are presented in table 23. These materials are examples of attempts to improve the magnetic properties not only by a change of composition, but also by the special technological process of producing amorphous and then crystallized ribbons. Inspecting this table one can thus conclude that coercivity of the alloys can be increased with Ga and/or Zr substitution. At the same time the data for H_c (coercivity field) and H_a (anisotropy field) suggest that the microstructure is

W. SUSKI

Composition	$H_{\rm C}$	M_{s}	$\mu_{ m B}H_{ m a}$	$T_{\rm C}$
	(kOe)	(G)	(kOe)	(K)
Sm ₈ Fe ₈₃ Ti ₉	5.5	806	92	593
Sm ₈ Fe ₇₆ Ti ₈ V ₈	10.2	664	75	590
Sm ₈ Fe ₇₆ Ti ₇ CrV ₈	8.6	685	75	580
Sm ₈ Fe ₇₆ Ti ₇ ZrV ₈	10.3	674	80	588
$Sm_8Fe_{76}Ti_6Zr_2V_8$	9.4			591
Sm ₈ Fe ₇₆ Ti ₇ NbV ₈	9.4	608	80	585
Sm ₈ Fe ₇₆ Ti ₇ MoV ₈	8.1	596	80	570
Sm ₈ Fe ₇₆ Ti ₇ WV ₈	8.0	599	76	581
Sm ₈ Fe _{75.5} Ga _{0.5} Ti ₈ V ₈	10.7	692	76	590
Sm ₈ Fe ₇₆ GaTi ₈ V ₈	9.5			594
$Sm_8Fe_{75}Ga_2Ti_8V_8$	9.1			586

Table 23 m-temperature magnetic properties of Sm–Fe–Ti derivatives. Ribbons annealed at 800°C (also α -Fe)^a

^a Data from Wang and Hadjipanayis (1990).

a critical factor in achieving a high coercivity in this system. This conclusion is why there is extensive discussion of technological processes. Since the anisotropy field of 1:12 materials is frequently even larger than that for Nd–Fe–B derivatives, there is a good chance to increase the coercivities by applying various technological tricks.

3.3.5.2. *Technological processes.* The usual technological processes are sintering, rapid quenching and mechanical alloying. The rapidly quenched and crystallized samples are frequently multiphase, and the highest coercivity reported was 2.5 kOe (Schultz and Wecker 1988).

In the sputtering process, radio-frequency-heated (rf-heated) samples are directly crystallized onto heated substrates with an in-film-plane applied magnetic field, as well as first deposited in an amorphous form and then subsequently crystallized. As reported by Liu et al. (1988), Kamprath et al. (1988) and Cadieu et al. (1991), in the Nd–Ti–Fe and Sm–Ti–Fe systems a relatively soft magnetic ThMn₁₂-type phase near 85 at.% Fe with a coercivity of 1-2 kOe was observed. A higher coercivity of 7.8 kOe was obtained by overquenching of Sm_{0.95}Fe₁₀V₂ alloy and subsequently annealing it at 850°C (Pinkerton and van Wingerden 1989). The bulk magnets reported by the same authors, made by hot-pressing overquenched Sm_{0.89}Fe₁₀V₂ ribbons, reached 98% of the theoretical X-ray density, with the following bulk magnetic data: $H_c = 5.6 \text{ kOe}$, $B_r = 5.4 \text{ kG}$ and (BH)_{max} = 4.0 MGOe. The tetragonal structure was found by Singleton et al. (1988) after annealing melt-spun R₈Fe₆₄Ti₈ with R = Nd, Sm, Dy, Gd and R₈(Fe, Co)₇₆(V/Mo)₁₆ with R = Nd and Sm. The coercivity strongly depends on the microstructure and the highest value of H_c amounts to 2 kOe for the Sm–Fe–Ti system with a grain size of about 50 nm. In turn, high coercivity was reported by Singleton et al. (1989) in annealed

 $Sm(Fe, T)_{12}$ alloys with T=Ti, V, Al, Cu, Ga and Si containing small amounts of B and C ($H_c = 7.7$ KOe for Sm₁₀Fe₈₀Ti_{7.5}B_{2.5} sample). Strzeszewski et al. (1989) note that single-phase samples are obtained if rapidly quenched alloys of Sm_xFe_vTi_z-type with above mentioned additions are annealed above 800°C. For lower annealing temperature some samples exhibit a mixture of the TbCu₇-type phase with the ThMn₁₂ matrix. Examination of the derivatives of $RFe_{10}Ti$ alloys (Zhao et al. 1988) shows that rapidly quenched (splat-cooled or melt-spun) $Nd_x Dy_{1-x}Fe_{10}Ti$ samples are nearly single-phase and become multiphase upon heating. Also, Cochet-Muchy and Païdassi (1990) claim that the annealing of the Sm-Fe-Ti system causes precipitation of secondary phases. The appearance of metastable $TbCu_7$ -type phase was reported by Saito et al. (1988) for SmFe₁₁Ti-alloy ribbons for specific quenching rates (for the roll velocity $v_r > 4.3$ m/s). Coercivities of about 6 kOe were found for melt-spun $SmFe_{11.75}Ti_{1.04}$ with an optimal 10 min heat treatment at 800°C (Ding and Rosenberg 1989). Katter et al. (1990) relate the observed hard magnetic properties to the metastable (ω) phase in melt-spun Sm-Fe-Ti alloys. This phase is responsible for a coercivity of about 50 kOe. The formation of the ThMn₁₂-type phase has some influence on formation of the ω phase. The hardening process by annealing of Sm(Fe, Co)11Ti (Ding and Rosenberg 1990a) and Sm-Fe-V and Sm-(Fe, Co)-V (Ding and Rosenberg 1990b) alloys gives an energy product above 10 MGOe and coercivities up to 0.9 T, as mentioned above.

Otani et al. (1990) produced model calculations for reproducing hysteresis loops of randomly oriented grains with uniaxial anisotropy. The conclusion is that a strong intergrain coupling is beneficial for developing coercivity if the Th Mn_{12} -type compounds form nanocrystalline alloys with uniaxial anisotropy. In turn, Sun et al. (1990) proposed a model for the coercivity which is based on an analogy with the random-anisotropy model of amorphous magnetism and which gives the correct magnitude of the coercivity.

Reviews on the method of mechanical alloying (MA) were presented by Schultz and Katter (1991), by Schultz et al. (1991a) and by Jing-tang Wang (1992). MA was first developed in the late 1960s and considerable progress has been achieved over the last 20 years. This method overcomes many of the limitations of conventional alloying and creates alloys of metals that are difficult or impossible to combine otherwise. MA uses an interdiffusional reaction, which is enabled by the formation of an ultrafine layered composite of particles during the milling process in a highenergy ball mill. The metal-powder particles are trapped by the colliding balls, heavily deformed and cold-welded, leading to characteristically layered particles. Further milling refines the microstructure more and more. Depending on the properties of starting powders and on the milling conditions, the interdiffusional reaction to form the alloy can either take place during the milling or during a following heat treatment. For the ternary Sm–Fe–T systems, e.g., MA initially produces amorphous or twophase (amorphous + α -Fe) material, which can be transformed into a microcrystalline intermetallic phase.

Schultz and Wecker (1988) reported on mechanical alloying and successive heat treatment at 800°C applied to $Sm_8Fe_{80}Mo_{12}$ and $Nd_8Fe_{82}Mo_{10}$ systems. After milling, the samples do not show any hard magnetic behavior ($H_c < 200$ Oe). Neither intermetallic

W. SUSKI

phases nor an amorphous phase are formed during the milling. The hard magnetic 1:12 phase is formed after a diffusion heat treatment of 1 hour at 600–900°C (annealing). The best results are found after reaction at 800–900°C. The maximum coercivities depend strongly on the sample composition. The lowest coercivity is obtained for the supposedly single-phase $Sm_8Fe_{82}Mo_{10}$ sample. The sample with the highest coercivity ($Sm_{12}Fe_{78}Mo_{10}$) is located within the three-phase field (1:12, 2:17 and a Sm-rich phase, which is thought to be Fe₃Sm). This sample exhibits a demagnetization behavior typical for a magnetically isotropic species with a remanence of 4.6 kG, a coercivity of 3.5 kOe and an energy product of 3.8 MGOe. A more intense milling facilitates the formation of the 1:12 phase with a maximum coercivity of 3.8 kOe for a "triple-phase" sample. The Nd-containing sample exhibits no coercivity, demonstrating that these Nd compounds have a planar anisotropy.

Schultz et al. (1990) observed a highest coercivity of 5.6 kOe for $Sm_{10}Fe_{80}Mo_5Ti_5$, and $Sm_{10}Fe_{50}Co_{30}Ti_{10}$ exhibits a remanence of 5.9 kG and $T_C = 868$ K, however, a lower coercivity. The best energy product of 5.1 MGOe was found for $Sm_{10}Fe_{70}Co_{10}Ti_{10}$. Taking into account the high anisotropy fields, the H_c values are rather disappointing if compared with those for Nd–Fe–B systems. A magnetically isotropic, resin-bounded $Sm_{15}Fe_{70}V_{15}$ sample mechanically alloyed and annealed, shows $H_c = 11.7$ kOe (record). A higher remanence of $H_r = 4.9$ kG, in turn, was detected for a $Sm_{12}Fe_{73}V_{15}$ sample prepared in the same way ($H_c = 10.6$ KOe and energy product 5.2 MGOe).

The Sm–Fe–Ti system, mechanically alloyed with additional annealing, was the subject of investigation by Schnitzke et al. (1990); the results are consistent with those reported by Schultz et al. (1990).

In crystallized films of $Sm_{19}Fe_{73}Ti_8$ (prereacted in MA process) Kamprath et al. (1988) found H_c up to 38.5 KOe at room temperature; $Sm_{20}Fe_{70}Ti_{10}$ is a mixture of a hard magnetic phase with unknown structure, the 1:12 phase, and residual α -Fe and α -Ti. H_c for such material reaches 50.6 kOe.

Schultz et al. (1990) found that the $Sm_{15}Fe_{70}V_{15}$ with H_c amounting to 11.7 kOe is also a mixture of the ThMn₁₂ and Fe₃Sm phases. This last phase separates the 1:12 grains as a grain-boundary phase. Initially prepared 1:12 materials with composition close to nominal exhibited coercivities up to about 5 kOe.

As mentioned above, in the MA materials the product frequently contains some additional phases like Fe₃Sm (orthorhombic PuNi₃-type) and, as reported by Schultz et al. (1991b), the hexagonal A₂ phase. The importance of the former phase was stressed above but the A₂ phase with a composition $Sm_{20}Fe_{70}Ti_{10}$ shows $H_c = 5.03$ T, $H_r = 3.0$ kG, whereas $H_c = 6.4$ T for composition $Sm_{26}Fe_{64}Ti_{10}$. The same authors noted that all magnetic materials obtained by the MA process show high or ultrahigh coercivities, but their saturation magnetization is relatively low. They claim, correctly, that the interstitial nitrides or carbides are more promising.

The above results show that various technological processes can improve the magnetic parameters of the $ThMn_{12}$ -type phases and their derivatives, but this research is still far from being finished, although recent results obtained on interstitials have attracted the interest of laboratories carrying out applied research.

3.4. Magnetic properties of actinide compounds with high content of transition element

It was already mentioned that only one binary compound of actinide metal $ThMn_{12}$ is known, but its magnetic properties have not been reported. The ternaries are known to exist in a bulk crystalline form with Fe, Co and Ni as transition element and with Si, Mo and Re as stabilizing components.

We do not believe that the actinide compounds, even if they exhibit favorable magnetic parameters, will find any application in future. Nevertheless, their properties are interesting from a fundamental point of view. The actinide contribution to the magnetism, the interaction between actinide and transition element, the distribution of the individual elements in different crystallographic positions, and the impact of the actinide on magnetic properties seem to be the most important scientific problems. Besides a systematic description of the actinide ternaries and pseudoternaries, we are going to devote special attention to these questions. Below we plan to describe the properties of ternaries and then to inspect how an admixture of additional components modifies the properties of basic compounds. According to this plan we first present the silicides of Fe, Co and Ni as the basic transition-metal components, then the materials containing other stabilizing elements than silicon, and finally pseudoternaries in which uranium is substituted by Y and Tb, and the transition element by other components.

3.4.1. Pure ternary compounds

The lattice parameters and magnetic data for the pure ternary compounds are collected in table 24.

3.4.1.1. $UFe_{10}Si_2$. The first investigated actinide compound with high concentration of transition element was UFe₁₀Si₂ (Suski et al. 1989, Berlureau et al. 1989). This compound turned out to be ferromagnetic below $T_C = 648$ K (see e.g. Zeleny et al. 1991), with saturation moment close to $1.6\mu_B$ /Fe atom (Andreev et al. 1992b). This value is estimated after subtraction of the contribution of α -Fe which is usually present in the majority of the ThMn₁₂-type ternaries. Moreover, UFe₁₀Si₂ exhibits considerable uniaxial anisotropy energy at room temperature: $H_a = 4.4$ T and $K_1 = 1.8$ MJ/m³, and at 4.2 K $K_1 = 3.0$ MJ/m³ (Andreev et al. 1995). These results were obtained on aligned polycrystals. The domain structure of this compound is much like that observed in Nd₂Fe₁₄B, and the domain wall energy amounts to 18 erg/cm² (Wysłocki et al. 1990). However, without special technological processes this material, like other ThMn₁₂-type intermetallics containing rare earths, exhibits a low remanence and coercivity as seen in fig. 53, even for field-preoriented samples (Baran et al. 1990).

Figure 54 (Andreev et al. 1991) shows that the homogeneity range of UFe_{12-x}Si_x extends over $1.0 \le x \le 3.0$. It is seen that the lattice parameters decrease almost according to Vegard's law, but both the Curie points and magnetic moments exhibit maxima, at $T_{\rm C} = 653$ K and $M_{\rm s} = 17.5\mu_{\rm B}/{\rm fu}$, respectively, for x = 2.

		-	-			10	•	
Compound	a (nm)	с (nm)	$M_{\rm s}$ $(\mu_{\rm B}/{ m fu})$	7 _C (K)	<i>Ө</i> (К)	$p_{\rm eff} \ (\mu_{\rm B})$	Remarks	Ref.
UFe ₁₀ Si ₂	0.8370	0.437		700				1
				648				2
			16.4				$E_{\rm a} = 2.2 \rm MJ m^{-1}$	3
							$E_{\rm DW} = 18 \rm erg/cm^2$	4
							⁵⁷ Fe ME	5
			17.8	650			S.C.	6
UCo ₁₀ Si ₂	0.824	0.463	8.5	550				5,7
							$E_{\rm DW} = 5 \rm erg/cm^2$	4
UNi10Si2	0.8185(5)	0.4686(3)			-120	3.46	$\chi_0 = 1.16 \times 10^{-3}$ emu mol,	8
							$\gamma = 100 \text{mJ/mol} \text{K}^2$	
							²⁹ Si NMR	9
UFe ₁₀ Mo ₂	0.850	0.476	7.7	250(?)				1
							⁵⁷ Fe ME	5
			8.7	210				6
UFe ₁₀ Re ₂	0.8541(2)	0.47141(11)		340				10

Table 24 Lattice parameters and magnetic data for $UM_{10}M'$ compounds

References

(1) Suski et al. (1989)

(2) Zeleny et al. (1991)

(3) Andreev et al. (1992b)

(4) Wysłocki et al. (1990)

(5) Baran et al. (1990)
(6) Gonçalves et al. (1994)

(7) Suski et al. (1991)(8) Suski et al. (1993d)

(9) Suski et al. (1993c)(10) Gueramian et al. (1991)



Fig. 53. Magnetization M (in arbitrary units) of UFe₁₀Si₂ (field-preoriented sample) versus magnetic field at 4.2 K (according to Suski et al. 1989, Baran et al. 1990, and Berlureau et al. 1991).

As concerns the distribution of Fe atoms, 57 Fe ME examination shows that the 8(i) positions are almost 100% occupied, the 8(j) positions are occupied about 93%, whereas only 60% of the 8(f) positions are occupied (Berlureau et al. 1991, Andreev et al. 1992b, Suski et al. 1992b, Vagizov et al. 1993). The location of the Fe atoms mainly in the 8(i) position is the most probable cause of the high magnetization and high Curie point; they are highest for the RFe₁₀Si₂ series, even higher than that determined for GdFe₁₀Si₂



Fig. 54. (Upper part) lattice parameters (*a*, c/a; left-hand scale; *c*: right-hand scale), (middle part) saturation magnetic moment p_s (right-hand scale), and (lower part) Curie points T_C (left-hand scale) for UFe_{12-x}Si_x alloys versus Si concentration *x*. For comparison T_C of the YFe_{12-x}Si_x system is also shown (Andreev et al. 1991).

 $(T_{\rm C} = 623$ K, Buschow et al. 1988, Q. Li et al. 1991). This is an indication of the U–Fe interactions in UFe₁₀Si₂. Another indication is presented in fig. 55, which compares the magnetization curves for the field-preoriented UFe₁₀Si₂ compound and YFe₁₀Si₂. One can see that the easy-direction curves are saturated at approximately 4 T, however the values of the molecular magnetic moment are different for both compounds and a larger moment is observed for the Y compound. At this point, one should note that the distribution of the Fe atoms in both compounds is much the same, as was shown in a ⁵⁷Fe ME experiment (Andreev et al. 1992c) and cannot be considered to be the cause of this difference. Andreev et al. (1992b,c) suggested that this difference results from a decrease in magnetic moment of the Fe sublattice due to a filling of the 3d band by electrons transferred from uranium. This is indicated by a decrease of hyperfine field found in ME measurements. The magnetic moment of U is estimated from magnetometric and ME results to be about $0.5\mu_{\rm B}$ coupled ferromagnetically with Fe. Use of single-crystal data (Gonçalves et al. 1994) gives a larger value of about $1.5\mu_{\rm B}$.

The evidence for a nonzero U orbital moment comes from a comparison of the hard-direction magnetization curves for both compounds, shown in fig. 55. The



Fig. 55. Magnetization of $YFe_{10}Si_2$ (squares) and $UFe_{10}Si_2$ (circles) versus magnetic field at 4.2 K measured for aligned powder samples. Open (solid) symbols correspond to field applied perpendicular (parallel) to the axis of alignment (Andreev et al. 1992b).

magnetocrystalline anisotropy of UFe₁₀Si₂ is considerably larger and there is a fieldinduced phase transition at around 4 T. Such a transition is rather common for harddirection magnetization curves in rare-earth intermetallics with high iron content and magnetic R components, $RFe_{12-x}M_x$, $R_2Fe_{14}B$ and R_2Fe_{17} . This transition is called a first-order magnetization process (FOMP) and it is explained by taking into account the phenomenological anisotropy constants K_1 , K_2 and K_3 (Deryagin et al. 1978, Asti and Bolzoni 1980).

Still another indication follows from magneto-optical investigations of UFe₁₀Si₂. In contrast to Brände et al. (1990), van Engelen and Buschow (1990) claim that the U sublattice contributes considerably to the Kerr effect.

Matar et al. (1994) have carried out theoretical band-structure investigations within the local-spin-density (LSD) approximation for UFe₁₀Si₂, UCo₁₀Si₂ and YFe₁₀Si₂ in order to understand (a) the magnetic moment carried by the U atom and the magnitude of its orbital part and (b) the role of Si in the bonding of these systems. For hypothetical UFe₁₂ with a spin-only magnetic moment, the moment of uranium ($\sim 2\mu_B$) is large with the spin aligned opposite to the Fe magnetic moment. This arises mainly from the polarization of 5f states ($-1.54\mu_B$) but there is a substantial contribution from 6d states ($-0.37\mu_B$). However, the inclusion of spin-orbit coupling produces a positive orbital moment on U mainly arising from f states, and this partly compensates the above-mentioned large negative spin-only moment with a resulting antiparallel spin alignment ($-0.68\mu_B$) between U and Fe. This statement contradicts the experimental results which indicate a positive contribution of the total magnetic moment of U to the magnetism of the UT₁₀Si₂ compounds. However, the calculated hybridization and the trends of evolution of the hyperfine fields

for UFe₁₀Si₂ and YFe₁₀Si₂ are in fair agreement with experimental data. As concerns the silicon contribution, it acts as a stabilizing agent of the crystal structure through hybridization between its s and p states and the s, p and d states of transition element. The presented calculations applied a simplified model of the electronic structure of the ternary silicides, and they only partly follow the experimental observations. Therefore, they are an inspiration for further theoretical considerations.

3.4.1.2. $UCo_{10}Si_2$. The magnetization curves of UCo₁₀Si₂ (fig. 56) show the typical ferromagnetic character of this compound below $T_{\rm C} \approx 550$ K with a saturation magnetization of about $8.5\mu_{\rm B}/{\rm fu}$ at 4.2 K (Baran et al. 1990, Suski et al. 1991), however this last value should be considered with care because saturation is not reached up to the highest applied field (14 T). One can see that both of the parameters are markedly lower than the corresponding values for UFe₁₀Si₂. For the saturation magnetization such difference is generally observed in the rare-earth compounds, however, the rare-earth compounds with Co usually exhibit higher Curie points than their iron analogs. This difference could be due to the poorer quality of $UCo_{10}Si_2$ in relation to $UFe_{10}Si_2$, but there may be another cause: for example, the band structure, which seems to cancel magnetic order in UNi10Si2, is sensitive to the 5f shell of uranium, which, in contrast to the 4f shell of the lanthanides, is at least partly itinerant. Also, the domain-wall energy for the Co compound is lower, amounting to 5 erg cm⁻², although the domain structures are of the same type as those for crystals with high uniaxial magnetocrystalline anisotropy (Wysłocki et al. 1990). As no FMR and ND results are yet available for UCo₁₀Si₂ one cannot propose any model for the distribution of the Co atoms in the crystal lattice. A comparison with $YCo_{10}Si_2$ is not straightforward, because the data concerning this compound are not in agreement. Buschow (1988a) denies the existence of this material whereas Lin et al. (1991) claim that it is ferromagnetic below 760 K and M_s at 1.5 K amounts to ~11.5 μ_B /fu, but the magnetic moment deviates from the *c*-axis, forming a canting angle. Although there is a strong



Fig. 56. Magnetization of $UCo_{10}Si_2$ versus magnetic field at 4.2 K (upper curve) and 300 K (lower curve). Circles correspond to increasing and crosses to decreasing magnetic field (Baran et al. 1990).

W. SUSKI

similarity in the iron distributions in the U and Y iron compounds we cannot assume that the same holds for the Co compounds. For $YCo_{10}Si_2$, on the basis of ND Lin et al. (1991) have proposed the following fractions for Co atoms in different crystallographic positions. The 8(i) site is preferred and contains about 41% of the total number of Co atoms whereas 29.5% is located on both 8(j) and 8(f) positions. A comparison of the differences in the values of the saturation moment of Co ternaries with U and Y with the same difference for the Fe compounds suggests AF coupling between Co and U sublattices.

3.4.1.3. $UNi_{10}Si_2$. UNi₁₀Si₂ is paramagnetic (Suski et al. 1993d) with a strong temperatureindependent susceptibility at lower temperature (Suski et al. 1993b) which at higher temperature shows a pronounced decrease. This decrease may result from CEF effects as mentioned by Moze et al. (1992).

The enhanced low-temperature electron specific heat coefficient, $\gamma \approx 100 \,\text{mJ}\,\text{mol}^{-1}\,\text{K}^{-2}$ (Suski et al. 1993d) is large enough to suggest the possibility of spin fluctuations (SF) in $UNi_{10}Si_2$. The absence of magnetism could result from the filling of the holes in the Ni 3d band by band electrons of U as observed in UNi5 (see e.g. Sechovsky and Havela 1988). At the same time another ternary U-Ni-Si compound, UNi₂Si₂, orders AF (Rebelsky et al. 1991). With respect to the element distribution, XRD results (Suski et al. 1993b) suggest that the Si atom is located exclusively in 8(j) positions, whereas ²⁹Si NMR (Suski et al. 1993c) indicates the possibility of Si atoms preferring to occupy either 8(f) or 8(j) sites. One should remember that XRD examination of UFe₁₀Si₂ and $UCo_{10}Si_2$ (Berlureau et al. 1991) showed that the ratios of 8(f) and 8(j) site occupancies by Si atoms are 3:1 and over 9:1, respectively. This last result shows that the analogy with YCo₁₀Si₂ does not hold. The fact that YNi₁₀Si₂ (Moze et al. 1992) and Y_{0.5}U_{0.5}Ni₁₀Si₂ (Suski and Wochowski, private communication) are nonmagnetic seems to suggest that the U ion is trivalent just as the Y ion because a substitution of Y by U does not affect the magnetic properties. As mentioned in sect. 3.3.1.1, the lanthanide silicides with Ni exhibit low-temperature magnetic ordering (Moze et al. 1992). This is evidence that the band electrons of the rare-earth atom fill up the Ni band, forming a nonmagnetic state in the sublattice of this element, and at low temperature the lanthanide 4f electrons are responsible for magnetic order. On the contrary, in the uranium compound the 5f electrons, due to hybridization with the conduction electrons, fill up the Ni band and consequently both the Ni and U sublattices appear to be nonmagnetic.

In turn we discuss the compounds in which an element other than Si is used to stabilize the Th Mn_{12} -structure type. Opposite to the rare-earth compounds, attempts at obtaining the uranium ternaries in bulk form were successful only with Mo and Re as stabilizing components.

3.4.1.4. $UFe_{10}Mo_2$. UFe₁₀Mo₂ was obtained simultaneously with UFe₁₀Si₂. However the properties of the former compound are puzzling. According to the first report (Suski et al. 1989) UFe₁₀Mo₂ exhibits ferromagnetic character below ~250 K with saturation magnetic moment about 7.5 μ_B /fu at 4.2 K and with a small hysteresis, which is nevertheless larger than that for the silicide. This result was recently confirmed by Gonçalves et al. (1994)

who found $T_{\rm C} = 210$ K and saturation magnetic moment at 10 K amounting to $8.7\mu_{\rm B}/{\rm fu}$. There is another high-temperature anomaly in the $\chi^{-1}(T)$ plot which suggests the presence of considerable amount of α -Fe, and XRD indicates a strong admixture of other phases. The results of Zeleny et al. (1991) show that UFe₁₀Mo₂ is very sensitive to annealing procedure. The $\chi_{\rm ac}(T)$ plot exhibits at temperatures above room temperature an anomaly corresponding to α -Fe (Zeleny et al. 1991). In turn, an examination of ⁵⁷Fe ME at 4.2 K excludes magnetic order (Baran et al. 1990). A preliminary ND experiment gives the same conclusion (Bourée-Vigneron, private communication).

As to other actinide compounds with a high concentration of a transition element, no thorium compounds are known, and therefore a comparison is made with YFe₁₀Mo₂. This compound exhibits ferromagnetic properties below 350 K (Buschow et al. 1988) and with the saturation moment at 4.2 K amounting to $13.0\mu_B/fu$ (Christides et al. 1993) aligned along the *c*-axis (Buschow et al. 1988) and a remanence of $3.23\mu_B/fu$ (zero-field-cooled sample) and $3.72\mu_B/fu$ (field-cooled sample) (Christides et al. 1993). Thus one can see that just as for other UM₁₀M' compounds, the magnetic parameters for the Y compound are higher than those of UFe₁₀Mo₂.

 $UFe_{10}Si_{1.75}Mo_{0.25}$ intermetallics were investigated in order to clarify the confusing results obtained for $UFe_{10}Mo_2$. Contrary to the reported multiphase composition of $UFe_{10}Mo_2$ the pseudoternary alloy was found to be single-phase (Suski et al. 1992b). Addition of a small fraction of Mo to the pure silicide decreases the Curie point to 547K (ME) and 565K (susceptibility) (Suski et al. 1992b). The magnetization curve at 4.2K exhibits a low magnetization and a less pronounced FOMP at low magnetic field. The general diminution of magnetic parameters in the case of Mo substitution in relation to pure silicide is most probably due to the Mo atoms occupying the 8(i) positions. Moreover, in the pseudoternary compound these sites are occupied by a fraction of the Si atoms as well, in contrast to $UFe_{10}Si_2$ in which the Si atoms are distributed among the 8(f) and 8(j) positions (Suski et al. 1992b).

3.4.1.5. $UFe_{10}Re_2$. The other crystalline compound in which the Si atoms are substituted is UFe₁₀Re₂. This material is ferromagnetic below 340K (Gueramian et al. 1991). Unfortunately, except for lattice parameters no data are available. Gueramian et al. (1991) stated that the rhenium substituting for iron enters mainly into the 8(i) sites, and this is probably the cause of the strong diminution of T_C in relation to the silicide.

The Curie point of $YFe_{10}Re_2$, 370 K (Gueramian et al. 1991), is only slightly higher than that of $UFe_{10}Re_2$, but that of $YFe_{10.8}Re_{1.2}$, is considerably higher at 460 K (Jurczyk 1990a). Because the saturation moment was not determined for $UFe_{10}Re_2$, we note that the parameters for $YFe_{10}Re_2$ are listed in table 21.

In addition to the crystalline compounds, amorphous materials of UFe₁₀M₂-type with M=Al, Ti, V, Cr, Ge, Sn and W have been prepared. They exhibit a much lower saturation magnetization than the corresponding crystalline silicide (H. Ratajczak, private communication) but unfortunately no detailed examination has yet been carried. The single exception is an investigation of the optical properties of UFe₁₀Ge₂ (Beznosov et al. 1992). Relative to amorphous iron this material exhibits a markedly lower optical

reflectivity and higher reflection magnetic circular dichroism. Normal to the film surface the magnetic field of saturation, H_s , at 16 K is ~3 T (for the crystalline silicide $H_s \approx 4$ T), and the coercive field $H_c \leq 0.2$ T.

3.5. Pseudoternary alloys

The pseudoternaries are discussed in the following order: we start with alloys in which uranium is substituted by another element, and then we will describe alloys in which the transition element is substituted for.

There are two systems in which U is substituted by rare-earth elements: Y and Tb. The first system is of special importance because as mentioned above, no Th compounds with high concentration of transition element are known and therefore Y can be used as a nonmagnetic diluent and its compounds as a standard with a nonmagnetic sublattice located at the 2(a) sites.

The $U_{1-x}Y_xFe_{10}Si_2$ system exists over the whole concentration range (Andreev et al. 1992c) and the lattice parameters determined at room temperature are presented in fig. 57 (lower panel). The smooth monotonic increase in both lattice parameters with increasing



Fig. 57. (Lower panel) lattice parameters (*a*: (lefthand scale, open circles; *c*: right-hand scale, open squares), and (upper panel) magnetic data (Curie points: left-hand scale, solid triangles; Fe magnetic moment calculated from hyperfine fields determined in ⁵⁷Fe ME experiment: right-hand scale, closed circles) in $U_{1-x}Y_xFe_{10}Si_2$ versus Y concentration x. The lines are guides to the eye (Andreev et al. 1992c).



Fig. 58. The distribution of the iron atoms in $U_{1-x}Y_xFe_{10}Si_2$ on different crystallographic positions versus Y concentration *x*, as determined by ⁵⁷Fe ME measurements. The lines are guides to the eye (Andreev et al. 1992c).

Y content reflects the fact that the atomic radius of this element is larger than that of uranium. The lattice expansion is isotropic; the c/a ratio is nearly constant for these alloys. A slight negative deviation from Vegard's law is typical for such solid solutions and can be related to the redistribution of the iron and silicon atoms during $U \leftrightarrow Y$ substitution, as shown by ⁵⁷Fe ME measurements and presented in fig. 58 (Andreev et al. 1992c). As mentioned above the distribution of iron atoms for both ternaries is close and we do not understand what causes the observed redistribution of components between the two endmembers. This redistribution has no influence on magnetic parameters, because as shown in fig. 57 the changes of the Curie points and Fe magnetic moment are monotonous, but exhibiting opposite tendencies. The decrease in $T_{\rm C}$ with increasing x can be explained by the magnetic state of uranium and the decrease in the U↔Fe exchange-interaction contribution to $T_{\rm C}$ for the alloys. The increase of magnetic moment calculated from the average hyperfine 57 Fe field $H_{\rm hf}$, assuming a field conversion factor of 14.5 T/ $\mu_{\rm B}$ proposed by Gubbens et al. (1988), is an indication of a modification of the magnetic moment of the iron sublattice (band structure) by uranium (hybridization?). Without such interaction the magnetic moment of the Fe sublattice should be independent of x. There is no contribution of Y because the calculated magnetic moment of the Fe sublattice amounts to $18.5\mu_{\rm B}$ /fu which is in fair agreement with magnetometric results for YFe₁₀Si₂ (Andreev et al. 1992b).

The $Tb_{1-x}U_xFe_{10}Si_2$ system is different from the $U_{1-x}Y_xFe_{10}Si_2$ alloys and exists as a single phase for x > 0.6. The alloys with lower uranium content contain about 5–8% α -Fe which disappears during prolonged homogenization. The lattice parameters are presented in fig. 59 (Andreev et al. 1993c). One can see that both lattice parameters decrease smoothly with increasing U concentration, resulting from the smaller metallic radius of U



Fig. 59. (Lower panel) lattice parameters (a, c) versus U concentration x, and (upper panel) magnetic phase diagram (T, x) of $Tb_{1-x}U_xFe_{10}Si_2$ (Andreev et al. 1993c). Dashed lines indicate the area in which an easy-cone configuration may be stable.

in comparison with that of Tb. Also, the magnetic moment measured on aligned powders along the axis of alignment depends monotonically on concentration. The thermomagnetic curves of $Tb_{1-x}U_xFe_{10}Si_2$ clearly demonstrate a difference between FC and ZFC curves which could be attributed to a spin-glass state. As can be seen from the upper part of fig. 59 (Andreev et al. 1993c) the Curie points of the $Tb_{1-x}U_xFe_{10}Si_2$ alloys increase with substitution of U for Tb as expected from the behavior of the parent ternaries. For x < 0.9 a T_{SR} is observed in some temperature intervals and in these intervals an easycone structure may be stable, however, they can result from a broadening of the first-order plane-axis transition due to inhomogeneity in the local atomic environment as well as to microscopic inhomogeneity of the samples which cannot be avoided in multicomponent alloys. The width of the temperature intervals is related to anisotropy constants. A rough estimation is that the U contribution to the magnetic anisotropy plays a secondary role in comparison with the Tb contribution, being smaller by one order of magnitude (1.3 MJ/m³ against 16 MJ/m³, respectively). This estimation contradicts a simple CEF consideration which indicates that the U ions in any configuration should provide a larger contribution



Fig. 60. (Lower panel) lattice parameters (*a*: righthand scale, triangles; *c*: left-hand scale, crosses), (middle panel) Curie points and (upper panel) saturation magnetization versus Co concentration *x* in UFe_{10-x}Co_xSi₂ alloys (Suski et al. 1991).

to the anisotropy than the Tb ions. This suggests that the CEF (localized) model cannot be applied to the uranium intermetallics.

We will now present the properties of the alloys in which magnetic Fe atoms are substituted by magnetic Co atoms. As one can see from fig. 60 (Suski et al. 1991) these alloys exist over the whole concentration range. Their lattice parameters decrease with increasing Co concentration in a monotonic way and, moreover, the *a* parameter decreases linearly. The addition of Co increases the Curie point, and a highest $T_C = 750 \text{ K}$ is observed for x = 6 (fig. 60) (Suski et al. 1991) as in many rare-earth systems in which Co addition increases T_C . The saturation magnetization does not show a change for $x \leq 2$, however, the precise determination of these values is difficult due to the rough estimation of the α -Fe contribution. The substitution of Co does not markedly change the remanence, but it increases the anisotropy and as a consequence saturation is observed under higher magnetic fields. Therefore the values of magnetization obtained by Berlureau et al. (1991) under a field of 2 T are far from saturation. The distribution of the Fe atoms over various crystallographic positions is presented in fig. 61. One can see that Fe atoms predominantly enter the 8(i) positions and the occupation decreases monotonously but



Fig. 61. Distribution of the Fe atoms in different crystallographic positions versus Co concentration x in UFe_{10-x}Co_xSi₂ alloys (Berlureau et al. 1991).

Fig. 62. Difference between saturation moment (right-hand scale, triangles) and Curie points (left-hand scale, circles) of UFe_{10-x}Co_xSi₂ (Suski et al. 1991) and YFe_{10-x}Co_xSi₂ (Lin et al. 1991) versus Co concentration x.

nonlinearly with increasing number of Co atoms. The number of Fe atoms in the 8(f) and 8(j) positions also decreases monotonously, but some redistribution is observed. To obtain any information about the uranium contribution we compare the results of magnetization measurements at 4.2 K obtained by Suski et al. (1991) for UFe_{10-x}Co_xSi₂ and by Lin et al. (1991) for YFe_{10-x}Co_xSi₂ alloys for which saturation magnetizatization was determined under magnetic field up to 7 T. The difference is presented in fig. 62 and is positive for low Co concentration, pointing to a ferromagnetic contribution of the uranium sublattice, but for x > 2 this contribution becomes negative, suggesting an antiferromagnetic coupling of the uranium sublattice. These results should be considered with proper caution,

keeping in mind the importance of technological processes and the α -Fe content for pseudoternaries. Although it is therefore difficult to compare the alloys produced in different laboratories, the differences presented in fig. 62 are too substantial to ignore them. Another cause of these differences may be the different types of magnetic structures or magnetocrystalline anisotropy. This last phenomenon was frequently observed in the rare-earth alloys mentioned in previous sections. However, a final conclusion about the uranium contribution can be presented only after successful ND experiments.

Substitution of Al has been introduced to improve the magnetic parameters (Suski et al. 1991). The absence of a high-temperature tail in the temperature dependence of magnetization in UFe₆Co₃AlSi₂, usually related to α -Fe, can be considered as an indication of the advantageous technological influence of Al. A diminution of the Curie point can be related to magnetic dilution by Al but also to the absence of α -Fe.

Finally, our discussion on the ThMn₁₂-type uranium pseudoternaries switches to the systems in which iron is substituted (diluted) by nonmagnetic components: Ni and Al. As will be shown, both these systems exist only for a limited composition range, and we do not know why this is so.

The range of existence of the UFe_{10-x}Ni_xSi₂ system extends up to x > 8. However, the alloys with $x \leq 8$ contain a small admixture of other, unidentified phases, and because of this the whole existence range $0 \le x \le 10$ was examined. As seen from fig. 63, the lattice parameters decrease almost linearly with increasing Ni concentration x, however, due to the considerable scatter of the experimental data it is difficult to decide whether the (a, c) vs. x plots follow Vegard's law (Suski et al. 1993b). Also, an uniform diminution of the occupation of individual crystallographic positions by Fe atoms is observed in ⁵⁷Fe ME (see fig. 63, Suski et al. 1993a). The magnetic properties of the UFe10-rNirSi2 alloys are summarized in fig. 64 (Suski et al. 1993a). There are two curves corresponding to the three magnetic phases. The lower curve is the high-temperature limit of a ferromagnetic phase, as determined by ME measurements and for x = 9.0 and 9.5 by ME and magnetometric methods. The upper curve, which is the low-temperature limit of the paramagnetic phase, is determined exclusively by magnetometric measurements, since Mössbauer spectra do not exhibit any splitting at temperatures above the lower curve. The phase existing between both curves has a ferromagnetic character, although the source of magnetism is a puzzle at present. The examination of samples with low Fe concentration (Suski et al. 1993c) seems to suggest that the high-temperature phase transition, $T_{\rm m}$, results from the presence of micrograins of free Ni with a concentration estimated to be about 3 and 7% for x = 9.5 and 9.0, respectively. However, high-resolution electron microscopy (HREM) examination of these materials does not confirm this possibility (Kępiński et al. 1994). Also, a decrease in $T_{\rm m}$ with increasing Fe concentration contradicts the possibility of the presence of free Ni. The low-temperature magnetization of these alloys exhibits saturation at a relatively low magnetic field of about 2 T (Suski et al. 1994) and also relatively high remanence. This easy saturation allows to assume that for 14 T one obtains the value of the saturation magnetic moment. Measurements at high magnetic field provide necessary data for the estimation of the contributions of the uranium and Ni/Co sublattices to magnetism of the $UFe_{10-x}(Co, Ni)_x Si_2$ alloys, as shown in fig. 65 (Suski


Fig. 63. (Lower part, open symbols) lattice parameters (right-hand scale; *a*: triangles; *c*: squares) and cell volume (left-hand scale; *V*: circles), and (upper part, solid symbols) distribution of the Fe atoms in 8(i) (circles), 8(j) (squares) and 8(f) (triangles) crystallographic sites versus Ni concentration *x* in UFe_{10-x}Ni_xSi₂. The lines are guides to the eye (Suski et al. 1993a,b).

Fig. 64. Magnetic phase diagram (T, x) for the UFe_{10-x}Ni_xSi₂ alloys (Suski et al. 1993a).



Fig. 65. The contribution of uranium and nickel/cobalt sublattices to the magnetic moment of the UFe_{10-x}(Ni, Co)_xSi₂ alloys versus Ni/Co concentration x (Suski et al. 1994).

et al. 1994). For the UFe_{10-x}Co_xSi₂ system an increase in the (U, Co) moment corresponds mainly to the Co moment, although a contribution of the U moment is also possible, particularly in the light of fig. 62. Note that the values presented are lower than reported in our previous publication (Suski et al. 1994), and particularly we do not plot at present the negative value of magnetic moment for $x \leq 2$. These discrepancies result from the fact that in the original figure both the Mössbauer data for the Fe sublattice and the "saturation" magnetization were taken from the paper of Berlureau et al. (1991). As mentioned above, their data for $UFe_{10-r}Co_xSi_2$ alloys in reality are far from saturation and this observation prompted us to use our magnetization data presented in fig. 60 (Suski et al. 1991). For the Ni system, this plot (fig. 65) is much more complicated. The value of the (U, Ni) sublattice moment exhibits a pronounced maximum for x = 4, amounting to about $4\mu_{\rm B}/{\rm fu}$. Since $UNi_{10}Si_2$ is nonmagnetic, one could expect that in the pseudoternaries the magnetic moment of the (U, Ni) subsystem is induced by the iron sublattice. These results together with earlier crystallographic and ME data suggest a change of band structure for alloys with x = 2-4. Unfortunately, one cannot extract only the contribution of either the U or the Ni sublattice using the techniques used today; this can only be done in neutron diffraction experiments. However, the highest magnetic moment observed for the uranium sublattice does not exceed $3\mu_{\rm B}$ (see e.g. Sechovsky and Havela 1988) and the observed value also indicates a contribution from the Ni subsystem. Nevertheless, this is an additional indication that the U sublattice contributes to the magnetism of the $ThMn_{12}$ -type compounds.

Attempts to introduce magnetic order through the substitution of Ni by Co have been unsuccessful. The UNi_{10-x}Co_xSi₂ system exists in an extremely narrow range for $x \le 0.5$. Some physical characteristics of UNi_{9.5}Co_{0.5}Si₂ are presented in fig. 66. One can see that both the temperature dependence of the magnetic susceptibility and the electric resistivity do not exhibit any indication of magnetic order. Only the high-temperature dependence of the magnetic susceptibility shows a change of slope at about 700 K, and



Fig. 66. (a) Magnetic susceptibility χ , (b) electric resistivity ρ , and (c) real part χ'_c of the ac magnetic susceptibility versus temperature. The inset shows high-temperature magnetic susceptibility χ_m versus temperature at 290–900 K for UNi_{9.5}Co_{0.5}Si₂ (Suski and Wochowski, private communication).

this was considered as additional proof of the precipitation of free Ni. However, below this temperature no ferromagnetic properties are observed (Suski and Wochowski, private communication).

In turn, the substitution of Cu for Ni in UNi₁₀Si₂ was planned to facilitate enhancement of the 5f-electron correlation, which manifests itself in the parent UNi₁₀Si₂ compound in which γ amounts to 100 mJ/mol K^2 . The UNi_{10-x}Cu_xSi₂ system exists up to $x \leq 2$ (Suski et al. 1993d) and Cu enters the 8(i) and 8(j) positions, although for x=1 an additional Si atom is found at the 8(i) site, which in turn disappears for x=2 (Suski et al. 1993b). The temperature dependence of the magnetic susceptibility of UNi₈Cu₂Si₂ has a complex shape, and two distinct temperature ranges in which the magnetic susceptibility of this



Fig. 67. (Upper panel) lattice parameters (a: left-hand scale, solid circles; c: right-hand scale, open circles), (middle panel) c/a, and (lower panel) magnetic data (magnetization measured along alignment axis, M: right-hand scale, solid triangles; Curie points $T_{\rm C}$: left-hand scale, solid squares) versus Al concentration x in UFe_{10-x}Al_xSi₂ (Andreev and Suski 1992).

compound follows the Curie–Weiss law are observed (Suski et al. 1993d). This could result from CEF effects, however, a more precise interpretation is difficult. The electric resistivity of this material depends very weakly on temperature, suggesting a strong effect of the band structure on the physical properties. In turn, there is no difference in the temperature dependence of specific heat of $UNi_{10}Si_2$ and UNi_9CuSi_2 at temperatures above 20 K and the lattice component of the total specific heat for both compounds is of the order of 85 and 90% at temperatures of 30 and 325 K respectively (Suski et al. 1993b).

The pseudoternaries which we are going to discuss are UFe_{10-x}Al_xSi₂ alloys. The system exists as a single phase for x < 3 only (Andreev and Suski 1992), however, as mentioned above, an admixture of Al removes α -Fe from these solid solutions (Suski et al. 1991). As can be seen from fig. 67 both lattice parameters increase with increasing Al content. The considerable nonlinearity, particularly of the c(x) plot, could be explained as a result of a preference for occupation of the 8(i) positions by Al atoms which was observed by ⁵⁷Fe ME measurements (Vagizov et al. (1993), see fig. 68). The $T_C(x)$ plot presented in fig. 67 is linear, just like the molecular magnetic moment vs. x measured along the alignment axis at 4.2 K in a field of 4 T. Such behavior is expected for substitution of iron by nonmagnetic aluminum. However, in spite of the linear $M_s(x)$ plot the field dependence of the molecular magnetic moment along and perpendicular to the axis of alignment at 4.2 K presented in fig. 69 indicates a change of anisotropy type. The character



Fig. 68. (a) Fe atom distribution in the 8(i), 8(j) and 8(f) sites, and (b) hyperfine field at 57 Fe measured at 14 K (right-hand scale, triangles) and magnetic moment of the Fe sublattices (left-hand scale, squares) versus Al concentration x in UFe_{10-x}Al_xSi₂ (Vagizov et al. 1993).

of the magnetization process for the alloys with x = 0 and 0.5 is the same and the energy of magnetocrystalline anisotropy becomes lower with increasing Al concentration. One can see that the compound $UFe_8Al_2Si_2$ is rather isotropic and that anisotropy occurs again for $x \leq 2.5$. This behavior confirms the change in anisotropy type with increasing aluminum content and reveals a basal-plane anisotropy for $x \ge 2.5$. Note that the distribution of Fe atoms presented in fig. 68a (Vagizov et al. 1993) shows that there is an equal occupation of the 8(f) and 8(i) sites for $x \approx 2.0$, and for $x \approx 1.5$ the occupation of the 8(i) and 8(f) positions is also fairly close. The same figure shows that aluminum enters mainly into 8(i) sites, replacing iron, and the substitution of half of the Fe atoms (x=2) leads to loss of the uniaxial anisotropy. The basal-plane contribution from the Fe 8(f) sites to the total magnetocrystalline anisotropy is large enough to compensate the uniaxial contribution not only from the semifilled Fe 8(i) sites but also from the uranium sublattice. The decrease in the Fe–Fe separation below a critical value for $x \ge 2$ is suggested as a cause of the change of anisotropy type (Vagizov et al. 1993). At the same time, the lack of change in anisotropy type in the LuFe_{10-x}Al_xSi₂ alloys suggests that the origin for this change in the uranium alloys must be sought in the U sublattice. Since, in UFe₁₀Si₂, the U sublattice gives a large uniaxial contribution to the magnetocrystalline anisotropy, the electronic state of U must change considerably to provide the basal-plane anisotropy for x > 2. This conclusion seems to be confirmed by the results presented in fig. 70: the difference between the magnetic moment of $UFe_{10-x}Al_xSi_2$ obtained from magnetization measurements (Andreev and Suski 1992) and magnetic moment of the Fe sublattice (57 Fe ME, Vagizov et al. 1993, fig. 68b) which increases with Al concentration x. It is interesting that the difference between the magnetizations of LuFe_{10-x}Al_xSi₂ (Andreev et al. 1993b) and UFe_{10-x}Al_xSi₂ (Andreev and Suski 1992) is fairly independent of x (fig. 70). Such an independence is





Fig. 70. Magnetic moment per uranium atom determined from: (a, circles) difference between saturation magnetization of $LuFe_{10-x}Al_xSi_2$ (Andreev et al. 1993b) and $UFe_{10-x}Al_xSi_2$ (Andreev and Suski 1992); (b, triangles) difference between magnetization of $UFe_{10-x}Al_xSi_2$ (Andreev and Suski 1992) and magnetic moment of the Fe sublattice (Vagizov et al. 1993, cf. fig. 68) versus Al concentration x.

Fig. 69. Molecular magnetic moment M of UFe_{10-x}Al_xSi₂ versus magnetic field measured on aligned powders, along (labeled 'e' for easy direction) and perpendicular to ('h' for hard direction) the axis of alignment at 4.2 K for different Al concentrations x (Andreev and Suski 1992).

a result of compensation between two mechanisms: the decreasing magnetic moment of Fe and the increasing magnetic moment of U.

The above results show the contribution of U ordering in high-3d-metal content intermetallics. However, due to a small expected magnetic moment of the uranium sublattice on the high ferromagnetic background of the 3d sublattice, these indirect indications are not convincing. Detailed neutron diffraction studies on single crystals are indispensable for direct confirmation of the existence of 5f and 3d ordered magnetism in 1:12 compounds.

4. Conclusion

The results we have presented on the magnetic and related properties of the ThMn₁₂type compounds suggest the following observations. The interest in the aluminides or other compounds with relatively low concentration of transition element is related to fundamental problems, whereas a lot of work done on the compounds with higher concentration of transition element, particularly their interstitial derivatives, is related to their potential user and commercial applications. As shown, our interest was limited to the fundamental problems also for this group of compounds.

Except for the various types of magnetic ordering related to both the f-electron element sublattice and/or the transition-element sublattice the $ThMn_{12}$ -type compounds, particularly aluminides, exhibit other intriguing phenomena, such as heavy-fermion-like behavior (e.g. $UCu_{4+x}Al_{8-x}$) or mixed valence (compounds of Ce and Yb).

A close inspection of the magnetic properties of the rare-earth and actinide compounds shows in principle their different behaviors. In the first group of materials, the 4f electrons exhibit localized character, which is confirmed by the value of the magnetic moment close to the free-ion value and by the different ordering temperatures of the lanthanide and transition-metal sublattices. On the contrary, in the actinide systems, namely in the uranium compounds (because we have only a minute amount of information concerning transuranium compounds), the uranium magnetic moment is apparently strongly influenced by hybridization and by the band structure of the transition element. As a result the ordering temperature of both sublattices is the same. We hope that this review provides the reader with convincing arguments for this idea as well as for the uranium sublattice contributing to magnetic ordering. Another cause of the similar, if not identical, ordering temperatures for both uranium and transition-element sublattices is the rather high transition temperature of the uranium sublattice in other compounds (for a review see Suski and Troć 1993), higher than in corresponding lanthanide compounds; this is related to strong exchange interactions.

Once again the need for single-crystal samples should be stressed. An example of interesting information which could be extracted from this type of samples is research on UFe₄Al₈ and UFe₁₀Si₂ (Paixão et al. 1994, Gonçalves et al. 1994). Because of tetragonal symmetry these compounds exhibit strong anisotropy. As mentioned in the Introduction we expected a much higher anisotropy in the uranium alloys but it appears that this is not always true. The example of (Tb, U)Fe₁₀Si₂ (Andreev et al. 1993b) shows that in these materials the anisotropy of the Tb sublattice is higher than that of the U sublattice.

Recently, some theoretical works have been published concerning the electronic structure and magnetic properties of the compounds discussed. They concern not only the materials with Y but even with uranium (see e.g. Matar et al. 1994). These preliminary calculations suggest that further progress can be accomplished in this difficult research area.

The large number of papers dedicated to the $ThMn_{12}$ -type compounds proves that the properties of these materials, either fundamental or technological, are the subject of vivid interest. This optimistic conclusion also suggests a less pleasant message for the author, namely that this text soon will be outdated.

Acknowledgements

I gratefully acknowledge the collaboration with my colleagues and coworkers: A. Baran, H. Drulis, T. Mydlarz, F.G. Vagizov and K. Wochowski. I also benefited from numerous discussions with A.V. Andreev and J. Gal.

References

- Akayama, M., H. Fujii, K. Yamamoto and K. Tatami, 1994, J. Magn. & Magn. Mater. 130, 99.
- Algarabel, P.A., and M.R. Ibarra, 1990, Solid State Commun. 74, 231.
- Amako, Y., H. Nagai, T. Nomura, H. Yoshie, I. Ogura, T. Shinohara and K. Adachi, 1992, J. Magn. & Magn. Mater. 104–107, 1451.
- Amako, Y., H. Nagai and K. Adachi, 1993, J. Phys. Soc. Jpn. 62, 3355.
- Anagnostou, M.S., and D. Niarchos, 1990, J. Magn. & Magn. Mater. 88, 100.
- Andreev, A.V., and W. Suski, 1992, J. Alloys & Compounds 187, 381.
- Andreev, A.V., V. Sechovsky, N.V. Kudrevatykh, S.S. Sigaev and E.N. Tarasov, 1988, J. Less-Common Met. 144, L21.
- Andreev, A.V., A.N. Bogatkin, N.V. Kudrevatykh, S.S. Sigaev and E.N. Tarasov, 1989, Fiz. Met. Metalloved. 68, 70.
- Andreev, A.V., M.I. Bartashevich, N.V. Kudrevatykh, S.M. Razgonyaev, S.S. Sigaev and E.N. Tarasov, 1990, Physica B 167, 139.
- Andreev, A.V., S.V. Andreev and E.N. Tarasov, 1991, J. Less-Common Met. 167, 255.
- Andreev, A.V., H. Nakotte and F.R. de Boer, 1992a, J. Alloys & Compounds 182, 55.
- Andreev, A.V., W. Suski and N.V. Baranov, 1992b, J. Alloys & Compounds 187, 293.
- Andreev, A.V., F.G. Vagizov, W. Suski and H. Drulis, 1992c, J. Alloys & Compounds 187, 401.
- Andreev, A.V., N.V. Kudrevatykh, S.M. Razgonyaev and E.N. Tarasov, 1993a, Physica B 183, 379.
- Andreev, A.V., Ye.V. Scherbakova, T. Goto and W. Suski, 1993b, J. Alloys & Compounds 198, 43.
- Andreev, A.V., W. Suski, T. Goto and I. Oguro, 1993c, Physica B 183, 385.
- Andreev, A.V., M.I. Bartashevich, H. Aruge Katori and T. Goto, 1995, J. Alloys & Compounds 216, 221.
- Arnold, Z., P.A. Algarabel and M.R. Ibarra, 1993, J. Appl. Phys. 73, 5905.
- Asano, S., S. Ishida and S. Fujii, 1993, Physica B 190, 155.
- Asti, G., and F.J. Bolzoni, 1980, J. Magn. & Magn. Mater. 20, 29.
- Asti, G., and S. Rinaldi, 1974, J. Appl. Phys. 45, 3600.
- Baran, A., 1988, J. Magn. & Magn. Mater. 76&77, 193.

- Baran, A., W. Suski and T. Mydlarz, 1983, in: Proc. Int. Conf. on Magnetism of Rare Earths and Actinides, eds. E. Burzo and M. Rogalski (Central Institute of Physics, Bucharest) p. 224.
- Baran, A., W. Suski and T. Mydlarz, 1984, J. Less-Common Met. 96, 269.
- Baran, A., W. Suski and T. Mydlarz, 1985, Physica B 130, 219.
- Baran, A., W. Suski, O.J. Zogał and T. Mydlarz, 1986, J. Less-Common Met. 121, 175.
- Baran, A., W. Suski and T. Mydlarz, 1987, J. Magn. & Magn. Mater. 63&64, 196.
- Baran, A., M. Łukasiak, W. Suski, J. Suwalski, H. Figiel, J. Opiła, K. Turek and T. Mydlarz, 1990, J. Magn. & Magn. Mater. 83, 262.
- Berezyuk, D.A., R.V. Skolozdra and O.I. Bodak, 1986, Vestnik Lvov. Univ., ser. khim. 27.
- Berezyuk, D.A., O.I. Bodak, F.G. Vagizov, K. Wochowski, W. Suski and H. Drulis, 1994, J. Alloys & Compounds 207&208, 285.
- Berezyuk, D.A., O.J. Bodak, W. Suski, K. Wochowski and T. Mydlarz, 1995, J. Magn. & Magn. Mater. 140-144, 931.
- Berlureau, T., B. Chevalier, L. Fournes and J. Etourneau, 1989, Mater. Lett. 9, 21.
- Berlureau, T., B. Chevalier, P. Gravereau, L. Fournes and J. Etourneau, 1991, J. Magn. & Magn. Mater. 102, 166.
- Beznosov, A.B., A.I. Galuza, N.F. Kharchenko, A.A. Milner, H. Ratajczak and W. Suski, 1992, Fiz. Nizk. Temp. 18(Suppl. S 1), 263.
- Bodak, O.I., and D.A. Berezyuk, 1983, The systems (Mo, W)–Fe–Ce, in: V Vsesoyuzn. Sov. po Khim. Tekhnolog. Mo i W., Tezisy Dokl., Part I (Ulan Ude) p. 78.
- Bodak, O.I., and D.A. Berezyuk, 1985, Dopov. Ak. Nauk Ukr. RSR ser. A (5), p. 83.
- Bodak, O.I., Ya.M. Kalychak and V.P. Skvorchuk, 1981, Dopov. Akad. Nauk Ukr. RSR Ser. A (10), p. 83.
- Bourée-Vigneron, F., M. Pinot, A. Oleś, A. Baran and W. Suski, 1990, Solid State Commun. 75, 929.
- Brabers, J.H.V.J., G.F. Zhou, F.R. de Boer and K.H.J. Buschow, 1993, J. Magn. & Magn. Mater. 118, 339.
- Brände, H., J. Schoenes, F. Hulliger and W. Reim, 1990, IEEE Trans. Magn. MAG-26, 2795.
- Burzo, E., M. Valeanu and N. Plugaru, 1992, Solid State Commun. 83, 159.

- Buschow, K.H.J., 1988a, J. Appl. Phys. 63, 3130.
- Buschow, K.H.J., 1988b, J. Less-Common Met. 144, 65.
- Buschow, K.H.J., 1989, J. Magn. & Magn. Mater. 80, 1.
- Buschow, K.H.J., 1991, J. Magn. & Magn. Mater. 100, 79.
- Buschow, K.H.J., and D.B. de Mooij, 1989, J. Less-Common Met. **155**, L9.
- Buschow, K.H.J., and A.M. van der Kraan, 1978, J. Phys. F 8, 921.
- Buschow, K.H.J., J.H.N. van Vucht and W.N. van den Hoogenhof, 1976, J. Less-Common Met. 50, 148.
- Buschow, K.H.J., D.B. de Mooij, M. Brouha, H.H.A. Smit and R.C. Thiel, 1988, IEEE Trans. Magn. MAG-24, 1611.
- Cadieu, F.J., H. Hegde, A. Navarathna, R. Rani and K. Chen, 1991, Appl. Phys. Lett. **59**, 875.
- Cadieu, F.J., A. Navarathna, R. Rani, H. Hegde, N.A. Bojarczuk and R.J. Gambino, 1993, J. Appl. Phys. 73, 6124.
- Cadogan, J.M., 1989, J. Less-Common Met. 147, L7.
- Cadogan, J.M., 1991, J. Alloys & Compounds 177, L25.
- Cadogan, J.M., H.S. Li, A. Margarian and J.B. Dunlop, 1993, Mater. Lett. 18, 39.
- Cao, L., L.S. Kong and B.G. Shen, 1992, Phys. Status Solidi (a) **134**, K69.
- Capehart, T.W., R.K. Mishra, G.P. Meisner, C.D. Fuerst and J.F. Herbst, 1993, Appl. Phys. Lett. 63, 3642.
- Chełkowska, G., A. Chełkowski and A. Winiarska, 1988, J. Less-Common Met. 143, L7.
- Chełkowski, A., and G. Chełkowska, 1988, J. Phys. F 18, L109.
- Chełkowski, A., E. Talik, J. Szade, J. Heimann, A. Winiarska and A. Winiarski, 1991, Physica B 168, 149.
- Cheng, S.F., V.K. Sinha, Y. Xu, J.M. Elbicki, E.B. Boltich, W.E. Wallace, S.G. Sankar and D.E. Laughlin, 1988, J. Magn. & Magn. Mater. 75, 330.
- Chin, T.S., W.C. Chang, H.C. Ku, C.C. Weng, H.T. Lee and M.P. Hung, 1989, IEEE Trans. Magn. MAG-25, 3300.
- Christides, C., D. Niarchos, A. Kostikas, H.S. Li, B.-P. Hu and J.M.D. Coey, 1989, Solid State Commun. 72, 839.
- Christides, C., A. Kostikas, A. Sunopolous, D. Niarchos and G. Zouganelis, 1990, J. Magn. & Magn. Mater. 86, 367.

- Christides, C., M.S. Anagnostou, H.S. Li, A. Kostikas and D. Niarchos, 1991a, Phys. Rev. B 44, 2182.
- Christides, C., H.-S. Li, A. Kostikas and D. Niarchos, 1991b, Physica B 175, 329.
- Christides, C., A. Kostikas, X.C. Kou, R. Grössinger and D. Niarchos, 1993, J. Phys.: Condens. Matter 5, 8611.
- Cochet-Muchy, D., and S. Païdassi, 1990, J. Magn. & Magn. Mater. 83, 249.
- Coehoorn, R., 1990, Phys. Rev. B 41, 11790.
- Coey, J.M.D., 1991, Phys. Scripta T 39, 21.
- Coey, J.M.D., and D.P.F. Hurley, 1992, J. Magn. & Magn. Mater. 104–107, 1098.
- Coey, J.M.D., H. Sun and D.P.F. Hurley, 1991, J. Magn. & Magn. Mater. 101, 310.
- Coldea, M., R. Coldea and G. Borodi, 1994a, IEEE Trans. Magn. MAG-30, 855.
- Coldea, R., M. Coldea and J. Pop, 1994b, IEEE Trans. Magn. MAG-30, 852.
- Cordier, G., E. Czech, H. Schäfer and P. Wolf, 1985, J. Less-Common Met. 110, 327.
- Darshan, B., and B.D. Padalia, 1984, J. Phys. C 17, L281.
- de Boer, F.R., Y.K. Huang, D.B. de Mooij and K.H.J. Buschow, 1987, J. Less-Common Met. 135, 199.
- de Mooij, D.B., and K.H.J. Buschow, 1987, Philips J. Res. 42, 246.
- de Mooij, D.B., and K.H.J. Buschow, 1988, J. Less-Common Met. 136, 207.
- Denissen, C.J.M., R. Coehoorn and K.H.J. Buschow, 1990, J. Magn. & Magn. Mater. 87, 51.
- Deportes, J., and D. Givord, 1976, Solid State Commun. 19, 845.
- Deportes, J., and D. Givord, 1977, Solid State Commun. 19, 845.
- Deportes, J., D. Givord, R. Lemaire and H. Nagai, 1977, Physica B 86-88, 69.
- Deryagin, A.V., N.V. Kudrevatykh and V.N. Moskalev, 1978, Phys. Status Solidi (a) 45, 71.
- Ding, J., and M. Rosenberg, 1989, J. Magn. & Magn. Mater. 80, 105.
- Ding, J., and M. Rosenberg, 1990a, J. Less-Common Met. 161, 263.
- Ding, J., and M. Rosenberg, 1990b, J. Less-Common Met. 161, 369.
- Ding, J., and M. Rosenberg, 1990c, J. Less-Common Met. 166, 303.
- Dirken, M.W., R.C. Thiel and K.H.J. Buschow, 1989, J. Less-Common Met. 146, L15.
- Doniach, S., 1977, Physica B 91, 231.

- Drulis, M., A. Baran, B. Staliński, W. Suski, R. Felten, F. Steglich and L. Pawlak, 1989, Thermochim. Acta 139, 219.
- Drzazga, Z., E. Talik, J. Heimann and J. Szade, 1994, IEEE Trans. Magn. MAG-30, 1006.
- Ermolenko, A.S., Ye.V. Scherbakova, G.V. Ivanova and E.V. Belozerov, 1990, Fiz. Met. Metalloved. 69, 59.
- Felner, I., 1980, J. Less-Common Met. 72, 241.
- Felner, I., and I. Nowik, 1978, J. Phys. Chem. Solids 39, 951.
- Felner, I., and I. Nowik, 1979, J. Phys. Chem. Solids 40, 1035.
- Felner, I., and I. Nowik, 1986a, J. Magn. & Magn. Mater. 54-57, 163.
- Felner, I., and I. Nowik, 1986b, J. Magn. & Magn. Mater. 58, 169.
- Felner, I., and I. Nowik, 1988, J. Magn. & Magn. Mater. 74, 31.
- Felner, I., M. Seh, M. Rakavy and I. Nowik, 1981a, J. Phys. Chem. Solids 42, 369.
- Felner, I., M. Seh and I. Nowik, 1981b, J. Phys. Chem. Solids 42, 1091.
- Felner, I., I. Nowik and M. Seh, 1983, J. Magn. & Magn. Mater. 38, 172.
- Fernando, A.S., J.P. Woods, S.S. Jaswal, B.M. Patterson, D. Welipitiya, A.S. Nazareth and D.J. Sellmyer, 1993, J. Appl. Phys. 73, 6919.
- Florio, J.V., R.E. Rundle and A.I. Snow, 1952, Acta Crystallogr. 5, 449.
- Fournier, J.-M., and R. Troć, 1985, in: Handbook on the Physics and Chemistry of the Actinides, Vol. 2, eds A.J. Freeman and G.H. Lander (Elsevier, Amsterdam) p. 29.
- Fujiwara, H., W.-L. Liu, H. Kadomatsu and T. Tokunaga, 1987, J. Magn. & Magn. Mater. 70, 301.
- Gal, J., H. Pinto, S. Fredo, M. Melamud, H. Shaked, R. Caciuffo, F.J. Litterst, L. Asch, W. Potzel and G.M. Kalvius, 1985, J. Magn. & Magn. Mater. 50, L123.
- Gal, J., H. Pinto, S. Fredo, H. Shaked, W. Schäfer, G. Will, F.J. Litterst, W. Potzel, L. Asch and G.M. Kalvius, 1987, Hyperfine Int. 33, 173.
- Gal, J., I. Yaar, E. Arbaboff, H. Etedgi, F.J. Litterst, K. Aggarwal, J.A. Pereda, G.M. Kalvius, G. Will and W. Schäfer, 1989, Phys. Rev. B 40, 745.
- Gal, J., I. Yaar, D. Regev, S. Fredo, G. Shami, E. Arbaboff, W. Potzel, K. Aggarwal, J.A. Pereda, G.M. Kalvius, F.J. Litterst, W. Schäfer and G. Will, 1990, Phys. Rev. B 42, 8503.

- Garcia, L.M., J. Bartolomé, P.A. Algarabel, M.R. Ibarra and M.D. Kuz'min, 1993, J. Appl. Phys. 73, 5908.
- Garcia, L.M., R. Burriel, F. Luis, E. Palacios, J. Bartolomé, E. Tomey, D. Fruchart, J.L. Soubeyroux and D. Gignoux, 1994, IEEE Trans. Magn. MAG-30, 595.
- Ge, S.-L., Q. Pan, G.Q. Yang, J.S. Zhong, Y. Yang, W. Tao, Y.-C. Yang and L.-S. Kong, 1992, Solid State Commun. 83, 487.
- Geibel, C., U. Ahlheim, A.L. Giorgi, G. Sparn, H. Spille, F. Steglich and W. Suski, 1990, Physica B 163, 194.
- Geng, M.M., R.Z. Ma, X. Chen and Z.X. Xu, 1991, Hyperfine Int. 68, 381.
- Gladyshevsky, E.I., O.I. Bodak and V.K. Pechersky, 1990, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 13, eds K.A. Gschneidner Jr and L. Eyring (Elsevier, Amsterdam) p. 1.
- Gonçalves, A.P., R.T. Henriques, G. Bonfait, M. Almeida and J.C. Spirlet, 1992, in: 22ièmes Journées des Actinides, Méribel, A3, p. 63.
- Gonçalves, A.P., J.C. Waerenborgh, G. Bonfait, M. Almeida, P. Estrele, M. Godinho and J.C. Spirlet, 1994, in: 24ièmes Journées des Actinides, Obergurgl, p. 8.
- Gong, W., and G.C. Hadjipanayis, 1992, IEEE Trans. Magn. MAG-28, 2312.
- Grössinger, R., R. Krewenka and K.H.J. Buschow, 1992, J. Alloys & Compounds 186, L11.
- Gubbens, P.C.M., A.M. van der Kraan and K.H.J. Buschow, 1985, Phys. Status Solidi (b) 130, 573.
- Gubbens, P.C.M., A.M. van der Kraan and K.H.J. Buschow, 1988, Hyperfine Int. 40, 389.
- Gubbens, P.C.M., G.J. Boender, A.M. van der Kraan and K.H.J. Buschow, 1991, Hyperfine Int. 68, 329.
- Gueramian, M., K. Yvon and F. Hulliger, 1991, J. Less-Common Met. 175, 321.
- Haije, W.G., J. Spijkerman, F.R. de Boer, K. Bakker and K.H.J. Buschow, 1990, J. Less-Common Met. 162, 285.
- Halevy, I., I. Yaar, E. Arbaboff, S. Fredo, D. Regev, J. Gal, W. Schäfer, G. Will, J. Jove, M. Pagés, G.M. Kalvius and W. Potzel, 1994, in: Proc. 24ièmes Journées des Actinides, Obergurgl, p. 82.
- Harrison, W.A., 1980, Electronic Structure and Properties of Solids (W.H. Freeman, San Francisco, CA) ch. 10.
- Hegde, H., R. Rani, A. Navarathna, K. Chen and F.J. Cadieu, 1991, J. Appl. Phys. 70, 299.

- Helmholdt, R.B., J.J.M. Vleggan and K.H.J. Buschow, 1988a, J. Less-Common Met. 138, L11.
- Helmholdt, R.B., J.J.M. Vleggan and K.H.J. Buschow, 1988b, J. Less-Common Met. 144, 209.
- Hu, B.-P., H.-S. Li, J.P. Gavigan and J.M.D. Coey, 1989a, J. Phys.: Condens. Matter 1, 755.
- Hu, B.-P., H.S. Li and J.M.D. Coey, 1989b, Hyperfine Int. 45, 233.
- Hu, B.-P., H.-S. Li, J.M.D. Coey and J.P. Cavigan, 1990, Phys. Rev. B 41, 2221.
- Hu, J., T. Wang, S.G. Zhang, Y.Z. Wang and Z.X. Wang, 1988, J. Magn. & Magn. Mater. 74, 22.
- Hu, J., T. Wang, H. Zhao, T. Ning, Z. Wang and X. Yang, 1989, Solid State Commun. 70, 983.
- Hu, J., Z. Dong, Y. Liu and Z. Wang, 1992, J. Magn. & Magn. Mater. 179, 89.
- Huang, R.-W., Z.-W. Zhang, B. Hu, J.-D. Kang, Z.-D. Zhang, X.K. Sun and Y.C. Chuang, 1993, J. Magn. & Magn. Mater. 119, 180.
- Huang, S.H., T.S. Chin, Y.S. Chen, S.K. Chen, C.-H. Lin, C.D. Wu and W.C. Chang, 1990, IEEE Trans. Magn. MAG-26, 1394.
- Hurley, D.P.F., and J.M.D. Coey, 1992, J. Phys.: Condens. Matter 4, 5573.
- Iandelli, A., and A. Palenzona, 1967, J. Less-Common Met. 12, 333.
- Ishida, S., S. Asano and S. Fujii, 1994, Physica B 193, 66.
- Jaswal, S.S., 1991, J. Appl. Phys. 69, 5703.
- Jaswal, S.S., 1993, Phys. Rev. B 48, 6156.
- Jaswal, S.S., Y.G. Ren and D.J. Sellmyer, 1990, J. Appl. Phys. 67, 4564.
- Jelonek, J., A. Chełkowski, W. Zarek, G. Chełkowska and A. Winiarska, 1990, J. Less-Common Met. 160, 273.
- Jurczyk, M., 1990a, J. Magn. & Magn. Mater. 89, L5.
- Jurczyk, M., 1990b, J. Less-Common Met. 166, 335.
- Jurczyk, M., 1990c, J. Magn. & Magn. Mater. 87, 1.
- Jurczyk, M., and D.D. Chistyakov, 1989, J. Magn. & Magn. Mater. 82, 239.
- Jurczyk, M., and K.V. Rao, 1991, J. Alloys & Compounds 177, 259.
- Jurczyk, M., G.K. Nicolaides and K.V. Rao, 1991a, J. Less-Common Met. 169, L11.
- Jurczyk, M., G.K. Nicolaides and K.V. Rao, 1991b, J. Appl. Phys. 70, 6110.
- Jurczyk, M., G.K. Nicolaides and K.V. Rao, 1991c, J. Magn. & Magn. Mater. 94, L6.
- Kamimori, T., W.L. Liu, H. Kadomatsu, M. Goto and H. Fujiwara, 1988, J. Phys. (France) 49, C8-381.

- Kamprath, N., L. Wickramasekara, H. Hegde, N.C. Liu, J.K.D. Jayanetti and F.J. Cadieu, 1988, J. Appl. Phys. 63, 3696.
- Kaneko, T., M. Yamada, K. Ohashi, Y. Tawara, R. Osugi, H. Yoshida, G. Kido and Y. Nakagawa, 1989, in: Proc. 10th Int. Workshop on Rare Earth Magnets and Their Application, Kyoto, p. 191.
- Katter, M., J. Wecker, L. Schultz and R. Grössinger, 1990, Appl. Phys. Lett. 56, 1377.
- Kępiński, L., W. Suski and K. Wochowski, 1994, J. Alloys & Compounds 213&214, 520.
- Kim-Ngan, N.H., P.E. Brommer and J.J.M. Franse, 1994, IEEE Trans. Magn. MAG-30, 837.
- Kirchmayr, H.R., 1969, Z. Angew. Phys. 27, 18.
- Kockelmann, W., W. Schäfer, G. Will, P. Fischer and J. Gal, 1994, J. Alloys & Compounds 207&208, 311.
- Koterlin, M.D., B.S. Morokhivskii, I.D. Shcherba and N.V. German, 1993, Ukr. Fiz. Zh. 38, 362.
- Krimmel, A., A. Loidl, C. Geibel, F. Steglich and G.J. McIntyre, 1992, J. Magn. & Magn. Mater. 103, 73.
- Kudrevatykh, N.V., M.I. Bartashevich, V.A. Reimer, S.S. Sigaev and E.N. Tarasov, 1990, Phys. Met. Metallogr. 70, 48.
- Kuz'ma, Yu.B., P.I. Kripyakevich and D.P. Frankevich, 1965, Izv. Akad. Nauk SSSR, Neorg. Mater. 1, 1547.
- Kuz'ma, Yu.B., B.M. Stelmakhovich and L.T. Galamushka, 1992, Izv. Ross. Akad. Nauk, Metally, p. 219.
- Lander, G.H., M.S.S. Brooks and B. Johansson, 1991, Phys. Rev. B 43, 13672.
- Le Roy, J., J.M. Moreau, C. Bertrand and M.A. Fremy, 1987, J. Less-Common Met. 136, 19.
- Li, H.-S., and J.M.D. Coey, 1991, in: Handbook of Magnetic Materials, Vol. 6, ed. K.H.J. Buschow (Elsevier, Amsterdam) p. 1.
- Li, H.-S., B.-P. Hu, J.P. Gavigan, J.M.D. Coey, L. Pareti and O. Moze, 1988, J. Phys. (France) 49, C8-541.
- Li, Q., Y. Lu, R.W. Zhao, O. Tegus and F.M. Yang, 1991, J. Appl. Phys. 70, 6116.
- Li, Z.W., X.Z. Zhou, A.H. Morrish and Y.C. Yang, 1990, J. Phys.: Condens. Matter 2, 9621.
- Li, Z.W., X.Z. Zhou and A.H. Morrish, 1991, J. Appl. Phys. 69, 5602.
- Liao, L.X., Z. Altounian and D.H. Ryan, 1991, J. Appl. Phys. 70, 6006.
- Lin, C., G.Z. Li, Z.-X. Liu, H.-W. Jiang, Z. Wan, J.-L. Yang, B.S. Zhang and Y.-F. Ding, 1991, J. Appl. Phys. 70, 6543.

- Liu, N.C., N. Kamprath, L. Wickramasekara, F.J. Cadieu and H.H. Stadelmaier, 1988, J. Appl. Phys. 63, 3589.
- Liu, W.L., H. Kadomatsu, H. Fujiwara, T. Kamimori and M. Goto, 1987, Solid State Commun. 63, 947.
- Luis, F., R. Burriel, L.M. Garcia, E. Palacios, J. Bartolomé, E. Tomey, D. Fruchart, J.L. Soubeyroux, S. Miraglia, R. Fruchart and D. Gignoux, 1994, IEEE Trans. Magn. MAG-30, 583.
- Lunkenheimer, P., M. Kramer, R. Viana, C. Geibel, A. Loidl, W. Suski, H. Ratajczak, I. Gościańska and T. Luciński, 1994, Phys. Rev. B 50, 9581.
- Luong, N.H., N.P. Thuy, L.T. Tai and N.V. Hoang, 1990, Phys. Status Solidi (a) 121, 607.
- Ma, R.H., M.M. Geng, Z.X. Xu and S.M. Pan, 1991, Hyperfine Int. 68, 385.
- Malik, S.K., S.K. Dhar, R. Vijayaraghavan, A. Monochar, B.D. Padalia and P.D. Prabhawalkar, 1981, in: Valence Fluctuations in Solids, eds L.M. Falicov, W. Hanke and M.B. Maple (North-Holland, Amsterdam) p. 245.
- Malozemoff, A.P., A.R. Williams, K. Terakura, V.L. Moruzzi and K. Fukamichi, 1983, J. Magn. & Magn. Mater. 35, 192.
- Malozemoff, A.P., A.R. Williams and V.L. Moruzzi, 1984, Phys. Rev. B 29, 1620.
- Matar, S.F., B. Chevalier and J. Etourneau, 1994, J. Magn. & Magn. Mater. 137, 293.
- Melamud, M., L.H. Benett and R.E. Watson, 1987, J. Appl. Phys. 61, 4246.
- Morariu, M., M.S. Rogalski, M. Valeanu and N. Plugaru, 1993, Mater. Lett. 15, 383.
- Moze, O., P.A. Algarabel, M.R. Ibarra, M. Solzi and L. Pareti, 1988a, Solid State Commun. 68, 711.
- Moze, O., L. Pareti, M. Solzi and W.I.F. David, 1988b, Solid State Commun. 66, 465.
- Moze, O., R. Caciuffo and K.H.J. Buschow, 1990a, Solid State Commun. 76, 331.
- Moze, O., R.M. Ibberson, R. Caciuffo and K.H.J. Buschow, 1990b, J. Less-Common Met. 166, 329.
- Moze, O., R.M. Ibberson and K.H.J. Buschow, 1990c, J. Phys.: Condens. Matter 2, 1677.
- Moze, O., R.M. Ibberson and K.H.J. Buschow, 1991, Solid State Commun. 78, 473.
- Moze, O., R. Caciuffo, K.H.J. Buschow and G. Amoretti, 1992, J. Magn. & Magn. Mater. 104– 107, 1391.
- Müller, A., 1988, J. Appl. Phys. 64, 249.
- Nagamine, L.C.C.M., and H.R. Rechenberg, 1992, J. Magn. & Magn. Mater. 104–107, 1277.

- Navarathna, A., H. Hegde, R. Rani, S.U. Jen and F.J. Cadieu, 1992, IEEE Trans. Magn. MAG-28, 2838.
- Naydyuk, Yu.G., O.E. Kvitnickaya, I.K. Yanson, W. Suski and L. Folcik, 1993, Low Temp. Phys. 19, 204.
- Neiva, A.C., F.P. Missel, B. Grieb, E.-Th. Henig and G. Petzow, 1991, J. Less-Common Met. 170, 293.
- Nowik, I., and I. Felner, 1983, in: Magnetism of Rare Earths and Actinides, eds E. Burzo and M. Rogalski (Central Institute of Physics, Bucharest) p. 24.
- Ohashi, K., T. Yokoyama, R. Osugi and Y. Tawara, 1987, IEEE Trans. Magn. MAG-23, 3101.
- Ohashi, K., Y. Tawara, R. Osugi and M. Shimao, 1988a, J. Appl. Phys. 64, 5714.
- Ohashi, K., Y. Tawara, R. Osugi, J. Sakurai and Y. Komura, 1988b, J. Less-Common Met. 139, L1.
- Ohashi, K., H. Ido, K. Konno and Y. Yoneda, 1991, J. Appl. Phys. 70, 5986.
- Okada, M., A. Kojima, K. Yamagishi and M. Homma, 1990, IEEE Trans. Magn. MAG-26, 1376.
- Okamoto, N., H. Nagai, H. Yoshie, A. Tsujimura and T. Hihara, 1987, J. Magn. & Magn. Mater. 70, 299.
- Otani, Y., H.-S. Li and J.M.D. Coey, 1990, IEEE Trans. Magn. MAG-26, 2658.
- Paixão, J.A., A.P. Gonçalves, M. Almeida, G. Bonfait, M. Godinho and P. Burlet, 1994, in: 24ièmes Journées des Actinides, Obergurgl, p. 101.
- Pareti, L., M. Solzi, G. Marusi, M.R. Ibarra and P.A. Algarabel, 1991, J. Appl. Phys. 70, 3753.
- Pearson, W.B., 1984, J. Less-Common Met. 96, 103; 115.
- Pinkerton, F.E., and D.J. van Wingerden, 1989, IEEE Trans. Magn. MAG-25, 3309.
- Popiel, E.S., W. Zarek and M. Tuszyński, 1989, Hyperfine Int. 51, 975.
- Popiel, E.S., W. Zarek and M. Tuszyński, 1990, Hyperfine Int. 54, 667.
- Ptasiewicz-Bak, B., A. Baran, W. Suski and J. Leciejewicz, 1988, J. Magn. & Magn. Mater. 76&77, 439.
- Qi, Q.-N., Y.P. Li and J.M.D. Coey, 1992, J. Phys.: Condens. Matter 4, 8209.
- Rath, J., and A.J. Freeman, 1975, Phys. Rev. B 11, 2109.
- Rauchschwalbe, U., U. Gottwick, U. Ahlheim, H.M. Mayer and F. Steglich, 1985, J. Less-Common Met. 111, 265.
- Rebelsky, L., H. Lin, M.F. Collins, J.B. Garrett, W.J.L. Buyers, M.W. McElfresh and M.S. Torikachvili, 1991, J. Appl. Phys. 69, 4807.

- Rogalski, M.S., M. Morariu, M. Valeanu and N. Plugaru, 1993, Solid State Commun. 87, 139.
- Saito, H., M. Takahashi and T. Wakiyama, 1988, J. Appl. Phys. **64**, 5965.
- Sakuma, A., 1992, J. Phys. Soc. Jpn. 61, 4119.
- Sakuma, A., 1993, J. Appl. Phys. 73, 6922.
- Sakurada, S., A. Tsutai and M. Sahashi, 1992, J. Alloys & Compounds 187, 67.
- Schäfer, W., and G. Will, 1983, J. Less-Common Met. 94, 205.
- Schäfer, W., G. Will, J. Gal and W. Suski, 1989, J. Less-Common Met. 149, 237.
- Schäfer, W., G. Will and J. Gal, 1991, Eur. J. Solid State Inorg. Chem. 28, 563.
- Schäfer, W., W. Kockelmann, G. Will, P. Fischer and J. Gal, 1994, J. Alloys & Compounds 207&208, 316.
- Scherbakova, Ye.V., A.S. Yermolenko, V.I. Khabrov, G.V. Ivanova and Ye.V. Belozerov, 1993, J. Alloys & Compounds 191, 79.
- Schnitzke, K., L. Schultz, J. Wecker and M. Katter, 1990, Appl. Phys. Lett. 56, 587.
- Schultz, L., and M. Katter, 1991, in: Supermagnets, Hard Magnetic Materials, eds J. Long and F. Grandjean (Kluwer Academic Publishers, Dordrecht) p. 227.
- Schultz, L., and J. Wecker, 1988, J. Appl. Phys. 64, 5711.
- Schultz, L., K. Schnitzke and J. Wecker, 1990, J. Magn. & Magn. Mater. 83, 254.
- Schultz, L., K. Schnitzke, J. Wecker and M. Katter, 1991a, Mater. Sci. & Eng. A 133, 143.
- Schultz, L., K. Schnitzke, J. Wecker, M. Katter and C. Kuhrt, 1991b, J. Appl. Phys. 70, 6339.
- Sechovsky, V., and L. Havela, 1988, in: Handbook of Magnetic Materials, Vol. 4, eds. E.P. Wohlfarth and K.H.J. Buschow (Elsevier, Amsterdam) p. 310.
- Shcherba, I.D., I.I. Kravchenko, M.D. Koterlin, A.P. Kushnir and A.P. Shpak, 1992, Metallofizika 14, 3.
- Singleton, E.W., J. Strzeszewski, G.C. Hadjipanayis and D.J. Sellmyer, 1988, J. Appl. Phys. 64, 5117.
- Singleton, E.W., J. Strzeszewski and G.C. Hadjipanayis, 1989, Appl. Phys. Lett. 54, 1934.
- Sinha, V.K., S.F. Cheng, W.E. Wallace and S.G. Sankar, 1989a, J. Magn. & Magn. Mater. 81, 227.
- Sinha, V.K., S.K. Malik, D.T. Adroja, J. Elbicki, S.G. Sankar and W.E. Wallace, 1989b, J. Magn. & Magn. Mater. 80, 281.
- Sinnemann, Th., M. Rosenberg and K.H.J. Buschow, 1989a, J. Less-Common Met. 146, 223.

- Sinnemann, Th., K. Erdmann, M. Rosenberg and K.H.J. Buschow, 1989b, Hyperfine Int. 50, 675.
- Sinnemann, Th., M.-U. Wisniewski, M. Rosenberg and K.H.J. Buschow, 1990, J. Magn. & Magn. Mater. 83, 259.
- Sokolovskaya, E.M., M.V. Raevskaya, A.I. Ilias, M.A. Pastushkova and O.I. Bodak, 1985, Izv. Ak. Nauk SSSR, Metally (5), p. 197.
- Solzi, M., L. Pareti, O. Moze and W.I.F. David, 1988, J. Appl. Phys. 64, 5084.
- Solzi, M., R.H. Xue and L. Pareti, 1990, J. Magn. & Magn. Mater. 88, 44.
- Stefański, P., 1990, Solid State Commun. 74, 731.
- Stefański, P., and A. Kowalczyk, 1991, Solid State Commun. 77, 397.
- Stefański, P., and A. Wrzeciono, 1989, Phys. Status Solidi (b) 151, K195.
- Stefański, P., A. Kowalczyk and A. Wrzeciono, 1989a, J. Magn. & Magn. Mater. 81, 155.
- Stefański, P., A. Szlaferek and A. Wrzeciono, 1989b, Phys. Status Solidi (b) 156, 657.
- Stefański, P., A. Kowalczyk and M. Budzyński, 1994, IEEE Trans. Magn. MAG-30, 669.
- Stelmakhovich, B.M., 1991, Visnik Lviv. Univ., ser.khim. 31, 20.
- Stelmakhovich, B.M., Yu.M. Kuz'ma and V.S. Babizhet'sky, 1993, J. Alloys & Compounds 190, 161.
- Stępień-Damm, J., A. Baran and W. Suski, 1984, J. Less-Common Met. 102, L5.
- Stewart, A.M., 1973, Solid State Commun. 12, 455.
- Stewart, A.M., and B.R. Coles, 1974, J. Phys. F 4, 458.
- Strzeszewski, J., Y.Z. Wang, E.W. Singleton and G.C. Hadjipanayis, 1989, IEEE Trans. Magn. MAG-25, 3309.
- Sun, H., Y. Otani, J.M.D. Coey, C.D. Meekinson and J.P. Jakubovics, 1990, J. Appl. Phys. 67, 4659.
- Sun, H., M. Akayama, K. Tatami and H. Fujii, 1993a, Physica B 183, 33.
- Sun, H., Y. Mori, H. Fujii, M. Akayama and S. Funahashi, 1993b, Phys. Rev. B 48, 13333.
- Suski, W., 1985, Physica B 130, 195.
- Suski, W., 1989, Physica B 155, 229.
- Suski, W., 1992, in: Proc. 2nd Int. Symp. on Physics of Magnetic Materials, Vol. I, ed. Shougong Zhang (International Academic Publishers, Beijing) p. 24.
- Suski, W., and R. Troć, 1993, in: Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, New Series, Group III.

Solid State Physics, Vol. 19f2, ed. H.P.J. Wijn (Springer, Berlin) p. 1.

- Suski, W., A. Baran and T. Mydlarz, 1989, Phys. Lett. A 136, 89.
- Suski, W., A. Baran, K. Wochowski and T. Mydlarz, 1991, J. Magn. & Magn. Mater. 95, L133.
- Suski, W., A. Baran, L. Folcik, K. Wochowski and T. Mydlarz, 1992a, J. Less-Common Met. 181, 249.
- Suski, W., F.G. Vagizov, H. Drulis, J. Janczak and K. Wochowski, 1992b, J. Magn. & Magn. Mater. 117, 203.
- Suski, W., F.G. Vagizov, K. Wochowski and H. Drulis, 1993a, J. Alloys & Compounds 201, 61.
- Suski, W., K. Wochowski, J. Janczak, T. Plackowski, K. Rogacki and D. Włosewicz, 1993b, Physica B 186–188, 764.
- Suski, W., K. Wochowski, A. Zygmunt, J. Janczak, B. Nowak, K. Niedźwiedź and O.J. Żogał, 1993c, J. Alloys & Compounds 199, 67.
- Suski, W., A. Zaleski, D. Badurski, L. Folcik, K. Wochowski, B. Seidel, C. Geibel and F. Steglich, 1993d, J. Alloys & Compounds 198, L5.
- Suski, W., K. Wochowski and T. Mydlarz, 1994, J. Alloys & Compounds 207&208, 290.
- Suski, W., K. Wochowski, A. Zalewski and T. Mydlarz, 1995, J. Alloys & Compounds 219, 275.
- Sysa, L.V., 1991, Visnik Lviv. Univ., ser. khim. 31, 15.
- Sysa, L.V., Ya.M. Kalychak, A. Bakar and V.M. Baraniak, 1989, Sov. Phys.-Crystallogr. 34, 744.
- Szytuła, A., 1991, in: Handbook of Magnetic Materials, Vol. 6, ed. K.H.J. Buschow (Elsevier, Amsterdam) p. 85.
- Talik, E., J. Szade and J. Heimann, 1993, Physica B 190, 361.
- Thuy, N.P., 1994, private communication.
- Tomey, E., O. Isnard, A. Fagan, C. Desmoulins, S. Miragha, J.L. Soubeyroux and D. Fruchart, 1993, J. Alloys & Compounds 191, 233.
- Tomey, E., M. Bacmann, D. Fruchart, S. Miraglia, J.L. Soubeyroux, D. Gignoux and E. Palacias, 1994, IEEE Trans. Magn. MAG-30, 687.
- Trygg, J., B. Johansson and M.S.S. Brooks, 1992, J. Magn. & Magn. Mater. 104–107, 1447.
- Vagizov, F.G., H. Drulis, W. Suski and A.V. Andreev, 1993, J. Alloys & Compounds 191, 213.
- Vagizov, F.G., W. Suski, K. Wochowski and H. Drulis, 1995, J. Alloys & Compounds 219, 271.
- van der Kraan, A.M., and K.H.J. Buschow, 1977, Physica B 86-88, 93.

- van Engelen, P.P.J., and K.H.J. Buschow, 1990, J. Magn. & Magn. Mater. 84, 47.
- Verhoef, R., F.R. de Boer, Z.D. Zhang and K.H.J. Buschow, 1988, J. Magn. & Magn. Mater. 75, 319.
- Wada, H., H. Nakamura, K. Yoshimura, M. Shiga and Y. Nakamura, 1987, J. Magn. & Magn. Mater. 70, 134.
- Wallace, W.E., and M.Q. Huang, 1992, IEEE Trans. Magn. MAG-28, 2312.
- Wang, F.C., and J. Gilfrich, 1966, Acta Crystallogr. 21, 746.
- Wang, Jing-tang, 1992, in: Proc. 2nd Int. Symposium on Physics of Magnetic Materials, Vol. 2, ed. Shougong Zhang (International Academic Publishers, Beijing) p. 441.
- Wang, Xian-zhong, B. Chevalier, T. Berlureau, J. Etourneau, J.M.D. Coey and J.M. Cadogan, 1988, J. Less-Common Met. 138, 235.
- Wang, Y.Z., and G.C. Hadjipanayis, 1990, J. Magn. & Magn. Mater. 87, 373.
- Weitzer, F., K. Hiebl, P. Rogl and Yu.N. Grin, 1990, J. Appl. Phys. 67, 3512.
- Williams, A.R., V.L. Moruzzi, A.P. Malozemoff and K. Terakura, 1983, IEEE Trans. Magn. MAG-19, 1983.
- Wysłocki, J.J., W. Suski and A. Baran, 1990, J. Less-Common Met. 163, 115.
- Wysłocki, J.J., W. Suski and K. Wochowski, 1994, IEEE Trans. Magn. MAG-30, 678.
- Xu, Xie, and S.A. Shaheen, 1993a, J. Magn. & Magn. Mater. 118, L6.
- Xu, Xie, and S.A. Shaheen, 1993b, J. Appl. Phys. 73, 5905.
- Yan Yu, Wang Xue-feng and Jin Han-min, 1994, J. Phys.: Condens. Matter 6, 2077.
- Yang, F.-M., Q.-A. Li, R.-W. Zhao, J.-P. Kuang, F.R. de Boer, J.P. Liu, K.V. Rao, G.K. Nicolaides and K.H.J. Buschow, 1991, J. Alloys & Compounds 177, 93.
- Yang, H., Q.-A. Li, N. Tang, Y. Li, O. Tegus, M.-J. Yu, F.M. Yang and F.R. de Boer, 1993, J. Magn. & Magn. Mater. 123, 317.
- Yang, Y.-C., L.S. Kong, S.H. Sun, D.M. Gu and B.P. Cheng, 1988a, J. Appl. Phys. 63, 3702.
- Yang, Y.-C., H. Sun, Z.-J. Zhang, T. Luo and J.-L. Gao, 1988b, Solid State Commun. 68, 175.
- Yang, Y.-C., L.-S. Kong, H. Sun, J.-L. Yang, Y.-F. Ding, B.S. Zhang, C.-T. Ye and L. Jin, 1990, J. Appl. Phys. 67, 4632.
- Yang, Y.-C., X.-D. Zhang, S.-L. Ge, Q. Pan, L.-S. Kong, H. Li, J.-L. Yang, B.S. Zhang, Y.-F. Ding and C.-T. Ye, 1991a, J. Appl. Phys. 70, 6001.

- Yang, Y.-C., X.-D. Zhang, L.-S. Kong, Q. Pan and S.-L. Ge, 1991b, Appl. Phys. Lett. 58, 2042.
- Yang, Y.-C., Q. Pan, X.-D. Zhang, Y. Yang, M.W. Zhang and S.-L. Ge, 1992, J. Appl. Phys. 61, 2723.
- Yang, Y.-C., X.-D. Zhang, S.-T. Dong and Q. Pan, 1993, J. Appl. Phys. 74, 6847.
- Yang, Y.C., 1981, Acta Metall. Sinica 17, 335.
- Yang, Y.C., B. Kebe, W.J. James, J. Deportes and W. Yelon, 1981, J. Appl. Phys. 52, 2077.
- Yellon, B.W., and G.C. Hadjipanayis, 1992, IEEE Trans. Magn. MAG-28, 2316.
- Zarechnyuk, O.S., and P.I. Kripyakevich, 1963, Sov. Phys.-Crystallogr. 7, 436.
- Zarechnyuk, O.S., and R.M. Rykhal, 1978, Dopov. Akad. Nauk Ukr. SSR Ser. A., p. 370.

- Zarechnyuk, O.S., R.M. Rykhal and M.Yu. Schtoyko, 1975, Vestnik Lvov. Univ. 17, 24.
- Zeleny, M., M. Rotter, W. Suski, A. Baran and F. Zounova, 1991, J. Magn. & Magn. Mater. 98, 25.
- Zeng, Y., X. Wu and X. Yan, 1991, Hyperfine Int. 68, 397.
- Zhang, L.Y., E.B. Boltich, V.K. Sinha and W.E. Wallace, 1989, IEEE Trans. Magn. MAG-25, 3303.
- Zhao, Z.R., Y.G. Ren, K.D. Aylesworth, D.J. Sellmyer, E.W. Singleton, J. Strzeszewski and G.C. Hadjipanayis, 1988, J. Appl. Phys. 63, 3699.
- Zolotukhin, O.A., V.V. Zabenko, T.I. Ivanova, S.A. Nikitin, V.V. Sergeev, I.V. Telegina and I.S. Tereshina, 1993, Vest. Mosk. Univ., Ser. Fiz., Astron. 34, 80.

Chapter 150

MAGNETIC PROPERTIES OF NONMETALLIC LANTHANIDE COMPOUNDS

L.K. AMINOV, B.Z. MALKIN and M.A. TEPLOV Kazan State University, 420008 Kazan, Tatarstan, Russian Federation

Contents

	List	of symbols	296
1.	Intro	oduction	297
	1.1.	Spatial structure of some dielectric	
		rare-earth crystal systems	301
2.	Inter	rnal electric and magnetic fields	306
	2.1.	Hamiltonians of the magnetic subsystem	
		in a crystal	306
	2.2.	Crystal field parameters	312
	2.3.	Stark spectrum of a lanthanide ion in a	
		static lattice	317
	2.4.	Electron-phonon interaction	326
	2.5.	Free energy of a crystal and	
		magnetoelastic interactions	329
	2.6.	Effective spin Hamiltonians	340
3.	Van	Vleck paramagnets	346
	3.1.	Magnetic susceptibility	346
	3.2.	Magnetoelastic properties and nonlinear	
		magnetic susceptibility	350
	3.3.	NMR and local magnetic fields in	
		crystals	362
		3.3.1. Distinctive features of NMR of	
		the host lanthanide ions	362
		3.3.2. NMR of diamagnetic ligands	369
		3.3.3. Magnetic resonance line shape	
		for nuclei of Van Vleck ions	373
	3.4.	Nuclear magnetic relaxation and nuclear	
		acoustic resonance	377
		3.4.1. Effects of thermally excited 4f-	
		states on NMR spectra	377
		3.4.2. Nuclear relaxation mechanisms	379
	3.5.	Influence of point defects on local	
		magnetic properties	387
		3.5.1. EPR of impurity paramagnetic	• • •
		ions	387

	3.5.2. Spin-lattice relaxation of impurity	
	lanthanide ions	392
	3.5.3. Local distortions of a crystal	
	lattice due to impurity ions	396
	3.6. Nuclear magnetic cooling	399
	3.7. Nuclear magnetic ordering	401
4.	Ferro- and antiferromagnets	402
	4.1. Paramagnetic susceptibility	402
	4.2. Magnetic ordering and critical	
	phenomena	407
	4.3. Electric field effects	425
	4.4. Magnetoelastic phenomena	428
	4.5. Magnetic resonance	439
	4.5.1. Magnetic resonance spectra	439
	4.5.2. Transient processes in internal	
	magnetic fields	445
	4.5.3. Magnetic resonance line shape	448
	4.6. Magnetic relaxation in ordered and	
	non-ordered phases	452
5.	Mixed crystals	457
6.	Rare earths in RBa ₂ Cu ₃ O _{6+r} compounds	471
	6.1. Crystal structure and mesoscopic phase	
	separation	471
	6.2. Inhomogeneous and homogeneous	
	broadening of the energy levels	483
	6.3. Effect of copper-oxygen paramagnetic	
	complexes on nuclear magnetic	
	relaxation	485
7.	Conclusion	491
	Acknowledgements	492
	References	492

List of symbols

A_{J}	constant of hyperfine interaction	$\mathcal{H}_{\mathcal{S}}$	spin Hamiltonian
$A_{\alpha\beta}(\mathbf{v})$	exchange integrals	$\mathcal{H}_{ ext{shf}}$	Hamiltonian of superhyperfine
B_{pq}	crystal field parameters (operator		interaction
	equivalent notation)	J	total angular momentum
$B^q_{p,\alpha\beta}, B^q_{p,\lambda}(\Gamma^j_i)$	parameters of orbit-lattice	$J_{\alpha\beta}(ij)$	parameters of the exchange
	interaction		interaction
$C(\Gamma_i^{nk}), C_{\alpha\beta\gamma\delta}$	isothermal elastic stiffness	I	nuclear spin
_	constants	k _B	Boltzmann constant
$D_{\alpha\beta}$	demagnetization factors	$\boldsymbol{M}, \boldsymbol{M}_0$	electron magnetization
\boldsymbol{E}_0	external electric field	$M_{0}^{(0)}$	spontaneous magnetization
е	magnitude of electron charge	m	nuclear magnetization
$e_{\alpha\beta}, e_{\lambda}(\Gamma_i^k)$	lattice strains	m_{λ}	mass of an ion in λ -sublattice
$\boldsymbol{e}(\boldsymbol{j}_a \boldsymbol{q}_0)$	unit vector of the acoustic wave	Ν	number of crystal cells
	polarization	n	number of magnetically
$e(\lambda q j)$	polarization vector of a phonon		equivalent ions in a cell
F	free energy of a crystal per unit	$O^q_p(oldsymbol{J})$	Stevens operator-equivalents
$G_{1}, G_{\sigma_{1}}, G_{\sigma_{2}}, G_{\sigma_{3}}$	cell parameters in the exchange	p_{λ}	electric dipole moment of an ion in the λ -sublattice
	charge model	$O_{\alpha\beta}(\lambda\lambda')$	Lorentz field factors
$G_{ij}(\Gamma)$	dimensionless constants of	2 up ()	phonon wave vector
	spin-phonon interaction	<i>q</i> ₁	ion charge (in units of e)
g _{αβ}	components of g-tensor	R,	ligand radius-vector
gı	Landé factor	s	electron spin
H	magnetic field	$S(\Gamma^{nk}), S_{max}$	elastic compliance constants
H_0	external steady magnetic field	- (- 1), - аруд Тс	Curie temperature
$H_{0lpha}^{(\mathrm{c})}$	applied field components in	T T	superconducting critical
	crystallographic coordinate	- 6	temperature
	system	T _N	Néel temperature
H_1	radiofrequency magnetic field	$T_{\rm D}$	temperature of structural phase
$H_{loc}(\lambda)$	local magnetic field on		transition
н	Hamiltonian of the lanthanide	T_{1}, T_{2}	nuclear relaxation times
, ce	ion in an electric field	υ	unit cell volume
$\mathcal{H}_{c,1}$	Hamiltonian of the lanthanide	$w(\lambda)$	internal displacement of a
	ion interaction with uniform		λ -sublattice
	lattice strains	$X(\lambda)$	radius vector of a lattice site λ in
\mathcal{H}_{e-ph}	Hamiltonian of electron-phonon	(M)	a unit cell M
	interaction	y(h)	vectors of a reciprocal lattice
$\mathcal{H}_{z}, \mathcal{H}_{H}$	electron Zeeman energy	α	paramagnetic shift tensor
\mathcal{H}_I	nuclear Zeeman energy	α_p, α_Q	ionic dipole and quadrupole
$\mathcal{H}_{ ext{hf}}$	Hamiltonian of hyperfine		scalar polarizabilities
- <i>i</i>	interaction	Γ_{i}	irreducible representation of the
\mathcal{H}_0	crystal field Hamiltonian		point-symmetry group
\mathcal{H}_{Q}	nuclear quadrupolar Hamiltonian	Υ1	nuclear gyromagnetic ratio

γ	effective gyromagnetic ratio	τ	electron relaxation time
	tensor	$ au_{c}$	correlation time
Δ	energy for f -electron excitation	X'	single-ion magnetic susceptibility
η_p	reduced matrix elements for ground multiplets of lanthanide	$\boldsymbol{\chi}^{(T)}$	temperature-dependent paramagnetic susceptibility
	ions	$\chi^{(0)}_{a6}$	Van Vleck susceptibility
$\Lambda_{0lphaeta}$	constants of the magnetic molecular field	$\widetilde{\omega_j(\boldsymbol{q})}$	phonon frequency of the <i>j</i> -th branch of vibrational spectrum
μ_{λ}	magnetic moment of an ion		with a wave vector \boldsymbol{q}
$\mu_{ m B}$	Bohr magneton	ω_0	magnetic resonance frequency
$\sigma_{\alpha\beta}$	stress tensor		
σ_p	shielding factors for crystal field		

1. Introduction

The aim of the present chapter is to summarize the available information on the magnetic properties of lanthanide compounds and to demonstrate that within the framework of the theoretical models developed until recently it is possible not only to describe but also to forecast the properties of these crystals. Specific magnetic and magnetoelastic properties of the crystals are determined by the localized electronic magnetic moments of lanthanide ions, regularly distributed in a crystal lattice, and by their interactions with each other and the surrounding ions. Other sources of magnetism in these substances are the nuclear spins of lanthanide ions and diamagnetic ligands as well as effective magnetic moments of paramagnetic impurities.

Practically all methods of physical experiments at low and ultralow temperatures – i.e. calorimetry, dilatometry, direct measurement of magnetic susceptibility and magnetization, gamma spectroscopy, EPR, NMR, resonance and nonresonance optical and acoustic spectroscopy, spectroscopy of thermal neutrons – are used in investigations of magnetic properties of the lanthanide crystals. These studies provide information not only of scientific but also significant applied value, particularly in problems of thermometry at low and ultralow temperatures and of magnetic cooling. Lately, in connection with the problem of high temperature superconductivity, its coexistence with magnetic ordering in rare-earth cuprates has evoked great interest in interionic magnetic interactions.

Lanthanide ions in crystals preserve their individuality; the values of free ion spin S, orbital momentum L, and total angular momentum J prove to be good quantum numbers, describing ionic states in crystals, and the splitting of the ${}^{2S+1}L_J$ multiplet by a crystal field is much smaller than intermultiplet intervals (Al'tshuler and Kozyrev 1972, Abragam and Bleaney 1970). The frequencies of electronic excitations within a ground multiplet, split by a crystal field, coincide with frequencies of the crystal lattice vibrations, and the resonance and nonelastic scattering of phonons on lanthanide ions determines the peculiarities of the spectrum and migration of low-frequency excitations in lanthanide compounds.

At low temperatures, when lanthanide ions are in their ground states, an external (or internal in a magnetically ordered state) magnetic field orients the magnetic moment of an ion and changes the spatial distribution of the 4f-shell density. Eventually an alteration of the interaction of 4f electrons with neighbouring ions occurs, which results in the displacements of these ions to new equilibrium positions and the alteration of interionic distances, i.e., the magnetic field affects the crystal lattice. The magnetostriction induced by an applied or internal field may reach giant values in lanthanide compounds (relative size changes of ~10⁻²) and this phenomenon is used for practical purposes (Belov 1987).

The lanthanide ion-ligand interaction undergoes changes at thermal excitations of a crystal as well. When the temperature rises, the population of the excited sublevels produces anomalies in the thermal expansion of crystals. Redistribution of electron density in a lanthanide crystal results in significant changes in the vibrational spectrum of a lattice, when variations in temperature occur. This is particularly evident for the anomalous temperature behaviour of elastic constants.

The ground multiplets of the lanthanide ions with an even number of electrons on unfilled 4f-shells – Pr^{3+} , Eu^{3+} , Tb^{3+} , Ho^{3+} , Tm^{3+} – are often split by a crystal field in such a manner that a singlet or nonmagnetic doublet appear to be the lowest energy levels, the excited levels being separated from the ground level by intervals of the order of $10-100 \text{ cm}^{-1}$. In such compounds the Van Vleck (VV) paramagnetism is pronounced, therefore they are usually called VV paramagnets.

Most of the VV paramagnets are characterized by the sharp anisotropy of their magnetic susceptibility, and specific temperature dependences of elastic and magnetoelastic properties. The ¹⁴¹Pr, ¹⁵⁹Tb, ¹⁶⁵Ho, and ¹⁶⁹Tm isotopes have a 100% abundance and a nonzero nuclear spin, so the compounds of these elements possess both electronic and nuclear magnetism, notably enhanced due to hyperfine interaction (Teplov 1977, Al'tshuler and Teplov 1978, Abragam and Bleaney 1983, Aminov and Teplov 1985, 1990). This enhancement is manifested in NMR spectra as enormous paramagnetic shifts of resonance lines and a sharp increase of the effective gyromagnetic ratio. Thus, $\gamma_{\rm eff} = 221 \gamma_I$ for the ¹⁶⁵Ho nucleus $(I = \frac{7}{2})$ in elpasolite Cs₂NaHoCl₆ (Bleaney et al. 1981b). Therefore it is possible to classify the magnetic resonance and relaxation of lanthanide ion nuclei in VV paramagnets as an intermediate phenomenon between ordinary NMR and EPR. The intermediate character of the resonance is also manifested in the extremely high anisotropy of effective γ -factors in uniaxial crystals, which may be illustrated by the angular dependence of the resonance field at a fixed spectrometer frequency (fig. 1). Such substances may be used for deep cooling of the nuclear magnetic system and also for observation of the nuclear magnetic ordering at more convenient experimental conditions than in usual nuclear magnets.

The ground states of ions with an odd number of f electrons in a crystal field are usually Kramers doublets with strongly anisotropic g-factors. The corresponding compounds are ferro- and antiferromagnets with comparatively low temperatures of magnetic ordering since the direct exchange between f electrons of neighbouring lanthanide ions is small. The compounds of lanthanide ions with an even number of electrons also belong to this type of magnets if their ground state is a magnetic doublet or triplet. Thus terbium



Fig. 1. Angular dependence of the resonance magnetic field of 169 Tm nuclei in a TmES crystal at a temperature of 4.2 K and a resonance frequency of 7.5 MHz.

Fig. 2. Molecular magnetic fields in the Ising ferromagnets TbES and DyES in the b'-c plane.

ethylsulfate (TbES) is an Ising ferromagnet with an ordering temperature of 0.24 K (Hirvonen et al. 1975). Above the ordering temperature a high degree of magnetic polarization can be achieved by applying an external magnetic field. Polarized and well localized magnetic moments of lanthanide ions give rise to a complicated but regular quasistatic picture of internal magnetic fields in the crystal (see fig. 2). NMR of diamagnetic ligands, localized at different positions in the unit crystal cell and therefore subjected to the influence of fields different in size and orientation, proves to be a sensitive method for studying internal fields. In such cases there exist certain peculiarities in forming nuclear free induction and spin echo signals.

Internal magnetic fields, induced by lanthanide ions both in VV paramagnets and ferroand antiferromagnets, fluctuate due to the thermal excitations of ions, which give rise to line shifts of the NMR of lanthanide ions and diamagnetic ligands, broadening of the lines and spin-lattice relaxation (SLR). The line shift, line width, and the rate of SLR at temperatures $k_{\rm B}T \ll \Delta$ inherently depend on temperature as $\exp(-\Delta/k_{\rm B}T)$, where Δ is the smallest excitation energy of a lanthanide ion (Aminov and Teplov 1985, 1990). When the temperature rises, higher energy states of the lanthanide ion may be displayed.

Many crystals of lanthanide compounds exhibit a cooperative Jahn-Teller (JT) effect, i.e. the change of crystal symmetry associated with electronic energy lowering due to the splitting of degenerate or nearly degenerate ground states of lanthanide ions (Gehring



Fig. 3. Four lower energy levels of Tm^{3+} ions in a LiTmF₄:Nd³⁺ crystal. The Tm^{3+} ions belong to (a) the first, (b) second and third, (c) fourth coordination spheres relative to the Nd³⁺ ion; (d) the same levels in the ideal (without impurities) LiTmF₄ crystal.

and Gehring 1975). An external magnetic field exerts a significant influence on the temperature of the structural phase transition in such systems, and sometimes it may suppress the transition completely.

Besides the JT effect some other interesting cooperative phenomena take place in concentrated lanthanide crystals. Thus Battison et al. (1975) have observed the splitting of an excited doublet of Ho^{3+} ion in the non-diluted compound $HoVO_4$ without lowering of the crystal symmetry. This phenomenon is described as "Davydov splitting" due to magnetic dipole–dipole and "phonon-field-mediated" interaction of the Ho^{3+} ions (Aminov 1981).

An important property of lanthanide atoms is the similarity of their chemical properties, conditioned by the small radius of the electronic f-shell and the configuration of the external s- and p-shells which is the same for all atoms. As a result their compounds form series including practically all lanthanide ions. Besides, mixed crystals are formed easily; crystals of lanthanide compounds are diluted easily by nonmagnetic La³⁺, Lu³⁺, and Y^{3+} ions. The crystal compounds of lanthanides inevitably contain some other lanthanide ions as impurity centers; moreover activation of crystals by impurities can be anticipated either with the purpose of imparting the necessary properties to a substance or as probes for investigating crystal characteristics. Intrusion of alien particles into the crystalline matrix appreciably changes its properties, especially near impurity centers. Thus purposeful investigations of these changes are an important element of the physics of real crystals. The crystal field, Stark splitting of energy levels, and, therefore, the effective magnetic moments of neighbouring lanthanide ions of a matrix undergo changes. Figure 3 illustrates an approximate picture of the shifts and splittings of the energy levels of Tm^{3+} ions in the LiTmF₄ crystal induced by the introduction of an Nd³⁺ impurity ion (Aminov et al. 1989, 1990b). Without due regard for the mentioned changes it is impossible to interpret a number of experimental data, first of all, the EPR linewidths and SLR times of impurity centers themselves.

The magnetic and magnetoelastic properties have been systematically investigated in rare-earth ethylsulfates (RES), tetrafluorides LiRF₄ with scheelite structure, RMO₄ crys-

tals having zircon structure (M = V, P, As), trifluorides RF₃, and lanthanide elpasolites. The available structural data on these systems are given below.

In ethylsulfates rare-earth ions are widely separated (≥ 7 Å), so the long range magnetic dipole-dipole interactions prevail in the magnetic coupling of the lanthanide ions. Fairly perfect ethylsulfate single crystals can be easily grown, and for this reason ethylsulfates have been used as model crystals for verification of different theoretical constructions and have been studied by optical and EPR methods for a long time. On the other hand, indirect exchange interactions of lanthanide ions in tetrafluorides play an important role. Lanthanide zircons are model objects in the theory of cooperative JT effects. In high-symmetry elpasolites lanthanide ions are localized in positions with cubic symmetry.

Lately high-temperature superconductors with rare-earth ions in their structure have been widely investigated. These compounds are based on antiferromagnetic dielectrics (yttrium-barium cuprates, cuprates of lanthanum or neodimium, etc.) having a distinctive lamellar structure which defines the peculiarities of magnetic interactions and magnetic ordering in the system of rare-earth ions.

Interpretation and systemization of the magnetic properties of lanthanide compounds are based on crystal field theory which has been repeatedly discussed in literature, in particular by Morrison and Leavitt (1982) in volume 5 of this Handbook. So we begin our chapter with a short account of crystal field theory in a comparatively simple form with a minimal number of initial parameters with a clear physical meaning. This immediately provides the interaction hamiltonians of 4f electrons with deformations and vibrations of the crystal lattice. Within the framework of this theory one can easily calculate the distortions of the crystal field near impurity ions. A clear idea of the nature of magnetic phenomena in simple dielectric lanthanide compounds is certainly useful for consideration of systems with a more complicated electron structure.

It should be noted also that some aspects of magnetic resonance in rare-earth compound crystals have been discussed in this Handbook by Barnes (1979) and Bleaney (1988) (vols. 2 and 11, respectively), so that the corresponding parts of the present chapter may be considered as a further extension of these works.

This review does not include metallic and intermetallic compounds, the magnetic properties of which have been discussed by Morin and Schmitt (1990), Purwins and Leson (1990), and also the compounds with transition metal and lanthanide ions (in particular, orthoferrites, garnet ferrites), in which case f-d exchange interactions must be considered in detail. The characteristics of rare-earth garnets are described in detail in a recent review by Kazei et al. (1991).

Thus we have outlined a number of important problems considered in the present chapter. The succession of their presentation is reflected in the contents.

1.1. Spatial structure of some dielectric rare-earth crystal systems

The ethylsulfate crystal $R(C_2H_5SO_4)_3.9H_2O$ has a rather complicated but well studied structure; the projection of its elementary cell on a plane normal to the main *c*-axis is presented in fig. 4. First Ketelaar (1939), then Fitzwater and Rundle (1959) determined



Fig. 4. (a) The unit cell of RES projected on a plane normal to the c-axis; (b) the nearest surroundings of a rare-earth ion in RES.

the space symmetry group P_63/m (C_{6h}^2) and positions of all heavy atoms by means of Xray diffraction. Broach et al. (1979), using the method of neutron diffraction, determined hydrogen atom coordinates in YES crystal at 110 K. Positions of these atoms in a Cartesian coordinate system are presented in table 1. (H4, H5 atoms belong to water molecules, H1, H2 to ethyl groups.)

Two molecules (128 atoms) are contained in a unit cell of an ethylsulfate. Magnetically equivalent lanthanide ions take positions with C_{3h} symmetry; their coordinates are $R_1(0, \frac{1}{3}a\sqrt{3}, \frac{1}{4}c)$ and $R_2(\frac{1}{2}a, \frac{1}{6}a\sqrt{3}, \frac{3}{4}c)$, where a and c are the lattice parameters. The values of the parameters for some ethylsulfates are as follows: YES (a=13.87 Å; c=7.007 Å), DyES (13.906 Å; 7.04 Å), ErES (13.910 Å; 7.05 Å). Rare-earth ions form chains along the crystal c-axis. The distance between ions within a chain equals ~7Å and that between the nearest ions of neighbouring chains is ~8.75 Å. A rare-earth ion is surrounded by nine water molecules and three ethyl groups CH₂-CH₃. The nearest surroundings are formed by nine O²⁻ ions of water molecules, three of them are in the plane with a rare-earth ion and the other six form a regular triangular prism.

Tetrafluorides LiRF₄ have a scheelite structure with the spatial symmetry group I4₁/a (C_{4h}^6) and local symmetry S₄ in rare-earth ion positions; a fragment of the lattice structure is presented in fig. 5. An elementary cell contains two formula units; the lattice points have the following coordinates (Thoma et al. 1970, Vishwamittar and Puri 1974, Als-Nielsen et al. 1975):

$$\begin{array}{lll} R_1(0,0,\frac{1}{2}) & R_2(0,\frac{1}{2},\frac{3}{4}) & \text{Li}(0,0,0) & \text{Li}(0,\frac{1}{2},\frac{1}{4}) \\ F_1(y,\frac{1}{2}-x,\frac{1}{4}+z) & F_2(x,\frac{1}{2}+y,\frac{1}{4}-z) & F_3(-x,\frac{1}{2}-y,\frac{1}{4}-z) & F_4(-y,\frac{1}{2}+x,\frac{1}{4}+z) \\ F_5(y,-x,-z) & F_6(x,y,z) & F_7(-x,-y,z) & F_8(-y,x,-z) \end{array}$$

the first two coordinates being in units of a and the third in units of c.

NONMETALLIC LANTHANIDE COMPOUNDS

Atom	x (Å)	y (Å)	z (Å)
Y1	0.000	8.008	1.752
Y2	6.936	4.004	5.255
H5A1	-1.567	5.963	3.267
H5A2	2.554	7.677	3.267
H5A3	0.990	10.387	3.267
H5B1	-0.240	6.102	4.038
H5B2	1.771	8.756 ⁻	4.038
H5B3	-1.532	9.170	4.038
H41	1.849	5.537	0.979
H42	1.215	10.845	0.979
H43	-3.064	7.642	0.979
H21	3.716	9.824	2.627
H22	-3.431	10.317	2.627
H23	-0.284	3.881	2.627
H1A1	3.933	11.907	1.752
H1A2	-5.343	9.465	1.752
H1A3	1.409	2.652	1.752
H1B1	5.353	11.622	2.593
H1B2	-5.808	10.837	2.593
H1B3	0.454	1.565	2.593

Table 1 Cartesian coordinates of Y and H atoms in the YES lattice (Broach et al. 1979) (x-axis is directed along a and z-axis along c)



Fig. 5. Part of an elementary cell of the LiRF₄ crystal with scheelite structure projected (a) on a plane normal to the *c*-axis, and (b) the nearest surroundings of a rare-earth ion in LiRF₄. Numbers in circles point out positions of ions relative to the a-b plane in units of the lattice constant *c*.



Fig. 6. An elementary cell of a RMO_4 crystal with zircon structure.

The lattice parameters a, c and the values x, y, z for some crystals are

Compound	a (Å)	c (Å)	x	у	Z
LiYF ₄	5.1668	10.733	0.2821	0.1642	0.0815
LiTbF4	5.1920	10.875	0.2802	0.1619	0.0810
LiYbF4	5.1335	10.588	0.2834	0.1661	0.0815

The Bravais lattice is a body-centered tetragonal, the nearest surroundings of a rare-earth ion are formed by two distorted fluorine tetrahedrons. The two nearest rare-earth ions are at a distance of ~ 3.75 Å.

The rare-earth compounds RMO₄ have a zircon-type crystal structure at room temperatures with space group I4₁/amd (D_{4h}^{19}) and local symmetry D_{2d} at the rare-earth lattice sites. This structure is shown in fig. 6. Coordinates of ions in an elementary cell are as follows:

$R_1(0,0,0)$	$R_2(0, \frac{1}{2}, \frac{1}{4})$	$M_1(0, 0, \frac{1}{2})$	$M_2(0, \frac{1}{2}, \frac{3}{4})$
$O_1(u,0,v)$	$O_2(-u,0,v)$	$O_3(0, u, -v)$	$O_4(0,-u,-v)$
$\mathcal{O}_5(u,\frac{1}{2},-v+\frac{3}{4})$	$\mathcal{O}_6(-u,\tfrac{1}{2},-v+\tfrac{3}{4})$	$O_7(0, u + \frac{1}{2}, v + \frac{3}{4})$	$O_8(0, -u+\frac{1}{2}, v+\frac{3}{4})$

The lattice parameters a, c and values of coordinates u, v for some crystals are given in table 2. More details may be found in papers by Aldred (1984), Will and Schäfer (1971), Lohmuller et al. (1973), Feuss and Kallel (1972), and Radhakrishna et al. (1981). The Bravais lattice in this case is also a body-centered tetragonal, the first two coordination spheres of a rare-earth ion consist of two fours of oxygen ions. Rare-earth ions are distributed with almost the same density as in tetrafluorides.

Trifluorides RF₃ (R = Gd, ..., Yb) belong to the Pnma (D_{2h}^{16}) space group, the Bravais lattice is orthorhombic, the point symmetry of rare-earth positions being $C_{1h} \equiv C_i$. An elementary cell contains four formula units, the coordinates of lattice points are as follows (three coordinates in units of *a*, *b*, *c*, correspondingly):

Compound	a (Å)	<i>c</i> (Å)	u	υ
YPO4	6.8840	6.0202	0.178	0.312
TmPO₄	6.8424	5.9895	0.1753	0.3405
ТЪРО₄	6.9437	6.0743	_	
GdAsO₄	7.1326	6.3578	-	
TbAsO₄	7.1020	6.3530	-	_
HoAsO₄	7.0550	6.3160	_	_
LuAsO₄	6.9492	6.2272	0.1833	0.3239
YVO₄	7.1193	6.2892	0.18523	0.32513
TbVO₄	7.1772	6.3289	0.1851	0.3261
TmVO₄	7.0693	6.2584	0.1870	0.32472
HoVO₄	7.1237	6.2890	0.1860	0.328
DyVO₄	7.1480	6.3067	0.1850	0.324

Table 2 Lattice constants of crystals with zircon structure

follows (Piotrowski et al. 1979):	
Lattice parameters a, b, c and positional parameters x_i, y_i, z_i for TbF ₃ and HoF ₃ a	are as
$F_{5-12}[\pm(x_2, y_2, z_2), \pm(x_2, \frac{1}{2} - y_2, z_2), \pm(\frac{1}{2} + x_2, y_2, \frac{1}{2} - z_2), \pm(\frac{1}{2} + x_2, \frac{1}{2} - y_2, \frac{1}{2} - z_2)]$	
$F_{1-4}[\pm(x_1,\frac{1}{4},z_1),\pm(\frac{1}{2}+x_1,\frac{1}{4},\frac{1}{2}-z_1)];$	
$R_1(x, \frac{1}{4}, z), R_2(\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z), r(R_3) = -r(R_1), r(R_4) = -r(R_2),$	

	a (Å)	b (Å)	c (Å)	x	Z	x_1	<i>z</i> ₁	<i>x</i> ₂	<i>y</i> ₂	<i>z</i> ₂
TbF3	6.513	6.940	4.384	0.368	0.061	0.522	0.584	0.165	0.066	0.384
HoF ₃	6.404	6.875	4.379	0.367	0.059	0.525	0.584	0.166	0.066	0.377

Rare-earth compounds A_2BRX_6 (A = Rb, Cs; B=Li, Na; X = F, Cl, Br, I) have an elpasolite structure [space symmetry group Fm3m (O_h^5)]. The cubic elementary lattice, shown in fig. 7, is characterized by a lattice parameter *a* and a relative distance *y* between the rare-earth ion and the X ligand, $y = R_X/a$. The lattice parameter *a* is known for a wide scope of compounds, and its nearly linear dependence on the atomic number of rare-earth ions at given A, B, X has been pointed out by Morss et al. (1970). The values of *a* at room temperature for some crystals, partly found by linear interpolation, are given in table 3. The values of parameter *y* are estimated for compounds Rb₂NaRF₆ as y=0.235-0.240 (Aleonard and Pouzet 1968, Bucher et al. 1974); for Cs₂NaErF₆, y=0.225; for Cs₂NaYF₆, y=0.250 (Vedrine et al. 1970); for Cs₂NaHoF₆, y=0.240 (Veenendaal et al. 1983); and for Rb₂NaHoF₆ at 207 K, y=0.250 (Ihringer 1982).



Fig. 7. An elementary cell of an A_2BRX_6 crystal with elpasolite structure.

Table 3 Lattice parameter a (Å) of some elpasolites A₂BRX₆ at room temperature

R	Cs ₂ NaRBr ₆	Cs ₂ NaRCl ₆	Cs ₂ KRF ₆	Rb ₂ NaRF ₆
Ce	11.508	10.946	9.610	9.08
Pr	11.46	10.912	9.596	9.06
Nd	11.421	10.889	9.58	9.04
Gd	11.370	10.792	9.51	8.952
Но	11.33	10.72	9.450	8.881
Er	11.32	10.704	9.43	8.859
Tm	11.30	10.686	9.41	8.839

Many compounds of the series undergo the structural phase transitions connected with rotations of octahedrons BX_6^{5-} and RX_6^{3-} . The PrAlO₃ compound, mentioned further in this chapter (sect. 3.3.1), in the high-temperature phase also has a cubic symmetry and its crystal structure looks like that in fig. 7 with A=Al; B, R=Pr; and X=O.

2. Internal electric and magnetic fields

2.1. Hamiltonians of the magnetic subsystem in a crystal

The total energy of a crystal containing lanthanides may be represented by the following operator which takes into account displacements of the lattice ions from their equilibrium

positions $X\begin{pmatrix}\lambda\\M\end{pmatrix}$ (λ , number of a sublattice; M, number of an elementary cell) at static and dynamic deformations:

$$\mathcal{H} = \mathcal{H}_{\text{lat}} + \mathcal{H}_{\text{ph}} + \mathcal{H}_1 + \mathcal{H}_2. \tag{1}$$

Here $\mathcal{H}_{lat} \equiv E_{lat}$ is the energy of elastic-deformed and polarized lattice; \mathcal{H}_{ph} is the vibration energy of ions; \mathcal{H}_1 is the electronic energy of noninteracting lanthanide ions; \mathcal{H}_2 is the energy of their pair interactions. Bearing in mind the investigation of the properties of both regular and mixed (diluted) crystals, we introduce occupation numbers $c_R(\lambda M)$ equal to unity when the lattice point λM is occupied by an R ion, or otherwise zero. Then the energy of lanthanide ions is written as

$$\mathcal{H}_{1} = \sum_{\mathbf{R}\lambda M} c_{\mathbf{R}}(\lambda M) \mathcal{H}_{\mathbf{R}}(\lambda M), \tag{2}$$

$$\mathcal{H}_{2} = \frac{1}{2} \sum_{\mathrm{RR}'} \sum_{\lambda M \lambda' M'} \mathcal{H}_{\mathrm{RR}'} \left(X \begin{pmatrix} \lambda & \lambda' \\ M & M' \end{pmatrix} \right) c_{\mathrm{R}}(\lambda M) c_{\mathrm{R}}'(\lambda' M'), \tag{3}$$

where

$$X\begin{pmatrix}\lambda & \lambda'\\ M & M'\end{pmatrix} = X\begin{pmatrix}\lambda\\ M\end{pmatrix} - X\begin{pmatrix}\lambda'\\ M'\end{pmatrix}$$

Assuming that the energies of $4f^n$ -electron shell multiplets are given, we represent the Hamiltonian \mathcal{H}_R of a single R ion as a sum of the following contributions: the interaction \mathcal{H}_0 with the static crystal field (ions forming a crystal are fixed at equilibrium positions), the interactions \mathcal{H}_E and \mathcal{H}_H with external electric (E_0) and magnetic (H_0) fields, the hyperfine (\mathcal{H}_{hf}) and superhyperfine (\mathcal{H}_{shf}) interactions, the energy \mathcal{H}_Q of the quadrupolar momentum of the R ion nucleus, the change \mathcal{H}_{e-1} of the crystal field energy at uniform deformation, and the interaction \mathcal{H}_{e-ph} with phonons:

$$\mathcal{H}_{\mathbf{R}} = \mathcal{H}_{0} + \mathcal{H}_{\mathbf{E}} + \mathcal{H}_{\mathbf{H}} + \mathcal{H}_{\mathbf{h}\mathbf{f}} + \mathcal{H}_{\mathbf{s}\mathbf{h}\mathbf{f}} + \mathcal{H}_{\mathbf{Q}} + \mathcal{H}_{\mathbf{e}-\mathbf{l}} + \mathcal{H}_{\mathbf{e}-\mathbf{p}\mathbf{h}}.$$
(4)

The magnetic properties of the lanthanide compounds are determined mainly by the relative positions and wave functions of the Stark sublevels of the ground multiplet. If only the energy spectrum of an R ion within the ground multiplet is of interest, one may restrict oneself to terms of \mathcal{H}_0 linear in single-electron operators, which are defined in the space of single-electron functions $|4fm\rangle = R_{4f}(r)Y_{3m}$ (R_{4f} is the radial wave function, Y_{1m} is the spherical function). The projection of \mathcal{H}_0 on the states of the ground multiplet is equal to

$$\mathcal{H}_0 = \sum_{p=2,4,6} \sum_{-p \leqslant q \leqslant p} B_{pq} \eta_p \mathcal{O}_p^q(\boldsymbol{J}),$$
(5)

where $O_q^q(J)$ are the Stevens' operators composed of the components of the angular momentum operator and corresponding to uniform spherical polynomials O_p^q of the

L.K. AMINOV et al.

direction cosines of the electron radius-vector \mathbf{r} . The complete list of Stevens' operator equivalents has been given by Hutchings (1964). The matrix elements of $O_p^q(\mathbf{J})$ are tabulated in monographs by Abragam and Bleaney (1970) and by Al'tshuler and Kozyrev (1972), and the reduced matrix elements for the ground multiplets of the R ions $\eta_2 = \alpha$, $\eta_4 = \beta$, $\eta_6 = \gamma$ are calculated by Stevens (1952). In what follows we shall not explicitly deal with the coefficients η_p ; they are supposed to be inserted into Stevens' operators $O_p^q(\mathbf{J})$.

In the theory of crystal fields the following spherical operators are often used:

$$C_{q}^{p} = \left(\frac{4\pi}{2p+1}\right)^{1/2} Y_{pq},$$
(6)

in terms of which the operator \mathcal{H}_0 takes the form

$$\mathcal{H}_0 = \sum_{pq} B_q^p C_q^p \tag{5a}$$

The complex crystal field parameters $B_q^p \left[B_{|q|}^p * = (-1)^q B_{-|q|}^p \right]$ are coupled to the real parameters B_{pq} by the equations

$$B_{p|q|} = (-1)^{q} a_{p|q|} \operatorname{Re} B_{|q|}^{p}, \qquad B_{p,-|q|} = -(-1)^{q} a_{p|q|} \operatorname{Im} B_{|q|}^{p}.$$
(7)

The numerical factors a_{pq} given in table 4 couple spherical operators to Stevens' polynomials:

$$a_{p|q|}O_{p}^{|q|} = C_{-|q|}^{p} + (-1)^{q} C_{|q|}^{p}, \qquad a_{p|q|}O_{p}^{-|q|} = i \left[C_{-|q|}^{p} - (-1)^{q} C_{|q|}^{p} \right],$$

$$a_{p0}O_{p}^{0} = C_{0}^{p}.$$
(8)

The energy change of an R ion in a crystal field, induced by an applied electric field E_0 and lattice deformation, may be expressed as a sum of single-electron operators as well. The effective electric dipole moment of the R ion in a lattice point with no inversion symmetry, is defined by parameters $b_{p\alpha}^{q}$ (the summation over repeated Greek indices, denoting the components of vectors, is implied in the following):

$$\mathcal{H}_{\rm E} = -\sum_{pq} b_{p\alpha}^{q} E_{0\alpha} O_{p}^{q}(\boldsymbol{J}).$$
⁽⁹⁾

The displacements of ions from the equilibrium positions at static and dynamic deformations of the lattice may be presented as

$$\Delta X_{\alpha} \begin{pmatrix} \lambda \\ M \end{pmatrix} = u_{\alpha\beta} X_{\beta} \begin{pmatrix} \lambda \\ M \end{pmatrix} + w_{\alpha}(\lambda) + \xi_{\alpha} \begin{pmatrix} \lambda \\ M \end{pmatrix};$$
(10)

where $u_{\alpha\beta} = \partial u_{\alpha}/\partial x_{\beta}$ are the components of the displacement tensor, considered in the theory of continuous medium elasticity, and $w(\lambda)$ is the displacement of the

sublattice λ . We express dynamical displacements ξ by means of phonon creation (a_{qj}^+) and annihilation (a_{qj}) operators in a regular lattice:

$$\xi_{\alpha} \begin{pmatrix} \lambda \\ M \end{pmatrix} = \frac{1}{\sqrt{Nm_{\lambda}}} \sum_{qj} e_{\alpha}(\lambda | qj) \exp\left[iqX \begin{pmatrix} \lambda \\ M \end{pmatrix}\right] Q(qj), \tag{11}$$

$$Q(qj) = \left(\frac{\hbar}{2\omega_j(q)}\right)^{1/2} (a^+_{-qj} + a_{qj}), \qquad (12)$$

where $\omega_j(q)$ is a frequency of the *j*-th branch of the vibrational spectrum, q is its wave vector, N is the number of crystal cells, $e(\lambda|q_j)$ is the polarization vector of a phonon, m_{λ} is the mass of an ion of the λ sublattice. The total energy of the phonons is

$$\mathcal{H}_{\rm ph} = \frac{1}{2} \sum_{\boldsymbol{q}j} \hbar \omega_j(\boldsymbol{q}) [2n_j(\boldsymbol{q}) + 1]$$

where $n_j(q) = a_{qj}^+ a_{qj}$ is the occupation number of the (qj) mode. The operator of electronphonon interaction linear on lattice normal coordinates Q(qj) is given as

$$\mathcal{H}_{e-ph}(\lambda M) = \frac{1}{\sqrt{N}} \sum_{qj} \sum_{pq} B_p^q(\lambda | qj) \exp\left[iq X \begin{pmatrix} \lambda \\ M \end{pmatrix}\right] Q(qj) O_p^q(J).$$
(13)

It should be noted that the linear electron-deformation interaction is explicitly involved when employing periodical boundary conditions for a crystal.

The distance between selected points in an elastic continuum is determined by the finite deformation tensor E:

$$E_{\alpha\beta} = e_{\alpha\beta} + \frac{1}{2}u_{\gamma\alpha}u_{\gamma\beta}, \qquad e_{\alpha\beta} = \frac{1}{2}(u_{\alpha\beta} + u_{\beta\alpha}), \tag{14}$$

where $e_{\alpha\beta}$ are the components of the infinitesimal deformation tensor. Introducing the tensor of finite rotations

$$\mathbf{\Omega} = (1+u)(1+2E)^{-1/2}$$
(15)

with components equal to

$$\Omega_{\alpha\beta} = \delta_{\alpha\beta} + \omega_{\alpha\beta} - \left(\frac{1}{2}\right)\omega_{\gamma\alpha}\omega_{\gamma\beta} + \left(\frac{1}{4}\right)(u_{\gamma\alpha}u_{\beta\gamma} - u_{\alpha\gamma}u_{\gamma\beta}) \tag{16}$$

up to second order in $u_{\alpha\beta}$, it is possible to present the increment of the vector $X\begin{pmatrix}\lambda\\M\end{pmatrix}$ in the laboratory coordinate system as

$$\Delta X \begin{pmatrix} \lambda \\ M \end{pmatrix} - w(\lambda) = [\Omega(1+2E)^{1/2} - 1] X \begin{pmatrix} \lambda \\ M \end{pmatrix}, \qquad (17)$$

and the antisymmetric tensor $\omega_{\alpha\delta} = \frac{1}{2}(u_{\alpha\beta} - u_{\beta\alpha})$ determines the rotation vector $\boldsymbol{\theta}$ with components $\theta_{\alpha} = -\frac{1}{2}e_{\alpha\beta\gamma}\omega_{\beta\gamma}$ ($e_{\alpha\beta\gamma}$ is the unit antisymmetric tensor).

Expanding the energy of the R ion in a crystal field in a series in the components of the displacement tensor, one can present the operator of electron-deformation interaction in the following form (Al'tshuler et al. 1985, Dohm and Fulde 1975):

$$\mathcal{H}_{e-l} = \mathcal{H}_{e-l}^{(1)} + \mathcal{H}_{e-l}^{(2)}, \tag{18}$$

$$\mathcal{H}_{e-1}^{(1)} = \sum_{pq} \left(B_{p,\alpha\beta}^{q} e_{\alpha\beta} + \sum_{\lambda} B_{p,\alpha}^{\prime q}(\lambda) w_{\alpha}(\lambda) \right) O_{p}^{q}(\boldsymbol{J}) + \mathbf{i}[\mathcal{H}_{0}, \boldsymbol{J}\boldsymbol{\theta}],$$
(19)

$$\mathcal{H}_{e-1}^{(2)} = \frac{1}{2} \sum_{pq} \left(B_{p,\alpha\beta}^{q} u_{\gamma\alpha} u_{\gamma\beta} + D_{p,\alpha\beta\gamma\delta}^{p} e_{\alpha\beta} e_{\gamma\delta} + \sum_{\lambda\lambda'} D_{p,\alpha\beta}^{\prime q} (\lambda\lambda') w_{\alpha}(\lambda) w_{\beta}(\lambda') + 2 \sum_{\lambda} D_{p,\alpha\beta\gamma}^{\prime \prime q}(\lambda) e_{\beta\gamma} w_{\alpha}(\lambda) \right) O_{p}^{q}(J)$$

$$+ i \sum_{\lambda} B_{p,\alpha\beta}^{q} e_{\alpha\beta} \left[O_{p}^{q}(J), \theta J \right] - \frac{1}{2} \left[\left[\mathcal{H}_{0}, \theta J \right] \theta J \right].$$

$$(20)$$

The terms of eqs. (19) and (20) containing the rotation angle θ are responsible for electron-rotation interaction. For simplicity we give in eq. (20) only those second-order terms in u which take into account the rotation about one of the crystallographic axes.

The main term of the interaction \mathcal{H}_{H} with an applied magnetic field H_0 is the Zeeman energy of an R ion electronic shell,

$$\mathcal{H}_{\rm Z} = g_{\rm J} \mu_{\rm B} H_0 J, \tag{21}$$

where μ_B is the Bohr magneton, and g_J is the Landé factor. If the nucleus of the R ion has a spin *I*, the Zeeman energy linked to it is

$$\mathcal{H}_{I} = -\gamma_{I} \hbar H_{0} I, \qquad (22)$$

as well as the energy of electric quadrupole interaction

pq

$$\mathcal{H}_{Q}^{(1)} = \frac{eQV_{zz}}{4I(I+1)} \left\{ [3I_{z}^{2} - I(I+1)] + \eta (I_{x}^{2} - I_{y}^{2}) \right\}.$$
(23)

Here γ_I is the nuclear gyromagnetic ratio, Q is the nuclear quadrupole moment, -e is the charge of an electron, V_{zz} is the component of the gradient of the ligand electric field, and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter of that gradient.

The interaction of the nucleus with the electronic shell (hyperfine interaction) is described by the operator $\mathcal{H}_{hf} + \mathcal{H}_{O}^{(2)}$, where

$$\mathcal{H}_{\rm hf} = A_{\rm J} J J, \tag{24}$$

$$\mathcal{H}_{Q}^{(2)} = e^{2} Q B_{J} \left[3(JI)^{2} + \left(\frac{3}{2}\right) JI - J(J+1) I(I+1) \right].$$
(25)

The constants A_J , B_J of the hyperfine structure are defined by the distribution of electronic density of the ion (Abragam and Bleaney 1970).

We restrict ourselves to the following terms in the interaction Hamiltonian of the R ion with nuclei of ligands (superhyperfine interaction):

$$\mathcal{H}_{\rm shf} = \sum_{\mathbf{v}} A_{\mathbf{v}\alpha\beta} J_{\alpha} I_{\mathbf{v}\beta},\tag{26}$$

where v is the index of a ligand.

The energy of a unit volume of deformed lattice in harmonic approximation is given by

$$\mathcal{H}_{\text{lat}} = \frac{1}{2} \widehat{C}_{\alpha\beta\gamma\delta} e_{\alpha\beta} e_{\gamma\delta} + \sum_{\lambda} b_{\alpha,\beta\gamma}(\lambda) w_{\alpha}(\lambda) e_{\beta\gamma} + \frac{1}{2} \sum_{\lambda\lambda'} a_{\alpha\beta}(\lambda\lambda') w_{\alpha}(\lambda) w_{\beta}(\lambda') - \sigma_{\alpha\beta} e_{\alpha\beta} - \frac{e}{v} E_{0\alpha} \sum_{\lambda} q_{\lambda} w_{\alpha}(\lambda),$$
(27)

where $\sigma_{\alpha\beta}$ is the tensor of external stress, q_{λ} is the ion charge, v is the volume of a cell. We consider explicitly only the ionic polarization of a lattice in an applied field E_0 ; inclusion of electronic polarization does not affect the qualitative results.

Introducing the potential energy of the lattice ϕ and the force constants

$$\phi_{\alpha\beta}\begin{pmatrix}\lambda & \lambda'\\ M & M'\end{pmatrix} = \frac{\partial^2\phi}{\partial X_{\alpha}\begin{pmatrix}\lambda\\ M\end{pmatrix} \partial X_{\beta}\begin{pmatrix}\lambda'\\ M'\end{pmatrix}},$$

we write the coefficients in eq. (27) as follows:

$$\widehat{C}_{\alpha\beta\gamma\delta} = [\alpha\gamma,\beta\delta] + [\alpha\delta,\beta\gamma] - [\alpha\beta,\gamma\delta],$$
(28)

$$[\alpha\beta,\gamma\delta] = -\frac{1}{2\nu} \sum_{M\lambda\lambda'} \phi_{\alpha\beta} \begin{pmatrix} \lambda & \lambda' \\ 0 & M \end{pmatrix} X_{\gamma} \begin{pmatrix} \lambda & \lambda' \\ 0 & M \end{pmatrix} X_{\delta} \begin{pmatrix} \lambda & \lambda' \\ 0 & M \end{pmatrix},$$
(29)

$$b_{\alpha,\beta\gamma}(\lambda) = \left(\frac{1}{v}\right) \sum_{M\lambda'} \phi_{\alpha\gamma} \begin{pmatrix} \lambda & \lambda' \\ 0 & M \end{pmatrix} X_{\beta} \begin{pmatrix} \lambda & \lambda' \\ 0 & M \end{pmatrix},$$
(30)

$$a_{\alpha\beta}(\lambda\lambda') = \begin{pmatrix} \frac{1}{v} \end{pmatrix} \sum_{M} \phi_{\alpha\beta} \begin{pmatrix} \lambda & \lambda' \\ 0 & M \end{pmatrix}.$$
 (31)

In the Hamiltonian $\mathcal{H}_{RR'}$ of the interaction between two R ions we shall single out terms responsible for the exchange, magnetic dipole–dipole and indirect (via the phonon field) interactions. The projection of the exchange interaction energy of ions R and R'

on the direct product of the spaces of the ground multiplet wave functions (with total moments J and J') has the form

$$\mathcal{H}_{ex} = \sum_{pp'} \sum_{qq'} A_{qq'}^{pp'} O_p^q(J) O_{p'}^{q'}(J').$$
(32)

It is practically impossible to obtain the analytical dependence of parameters $A_{qq'}^{pp'}(\mathbf{r})$ on the interionic distance \mathbf{r} . One may only state that they rapidly (not necessarily monotonously) decrease with the increase of \mathbf{r} . On the contrary, the magnetic dipole-dipole interaction is long-ranged:

$$\mathcal{H}_{d-d} = \left(\frac{g_J g_{J'}}{r^3}\right) \mu_{\rm B}^2 \left[\boldsymbol{J} \cdot \boldsymbol{J'} - \left(\frac{3}{r^2}\right) (\boldsymbol{J} \cdot \boldsymbol{r}) (\boldsymbol{J'} \cdot \boldsymbol{r}) \right]. \tag{33}$$

Energy of the interaction of R ions via the phonon field may be presented by means of Stevens' operators of an even rank (p, p'=2, 4, 6) in the form analogous to eq. (32) (see also Aminov and Kochelaev 1962). An explicit form of the corresponding parameters is given in sect. 2.5.

2.2. Crystal field parameters

Methods of construction of the effective crystal field Hamiltonian (5) for lanthanide ions in dielectrics have been repeatedly discussed in the literature (see, for instance, reviews by Newman 1971, Morrison and Leavitt 1982, Malkin 1987, Eremin 1989, Newman and Ng 1989, and Garcia and Faucher 1995). It is practically impossible to carry out a detailed quantum-mechanical study of a lanthanide ion spectrum in each specific case. Usually the crystal field parameters B_{pq} are determined by comparing the calculated ion spectrum with optical measurement data. However, this fitting procedure with transition frequencies makes it impossible to connect the resulting operator \mathcal{H}_0 with a definite (in particular, crystallographic) coordinate system, necessary for the description of magnetic characteristics of lanthanide ions. It should be noted, that even the drawing of complementary data on eigenfunctions of Hamiltonian \mathcal{H}_0 (g-factors, transition intensities), and accounting for variations in interelectron interactions in a crystal field (Eremin 1989, Newman and Ng 1989, Pilawa 1991) by introducing additional two-electron operators into eq. (5), cannot warrant a correct description of the ion spectrum, because, in particular, the electron-phonon interaction involves further displacements of Stark sublevels, comparable to multiplet energy differences in a static crystal field (Malkin 1963).

Since only information on the energy spectrum and wave functions of the ground multiplets is necessary for interpretation and prediction of magnetic properties of lanthanide compounds, and bearing in mind an essential role of electron-phonon interaction, we shall confine ourselves in this case to semiphenomenological models of the crystal field which allow one to represent parameters B_{pq} as definite functions of structural parameters of the crystal lattice. All the models developed until recently are

based on the assumption that single-particle interactions prevail (energy of 4f electrons localized within an R ion is represented as a sum of interaction energies with separate ions), and they differ by the number of fitting parameters and their functional dependence on interionic distances.

In analysis of the physical properties of lanthanide crystals the superposition model (Bradbury and Newman 1968, Newman 1971) is widespread. In this model a) the crystal field is formed only by the nearest neighbours (ligands) of an R ion; b) the interaction of the 4f electron with a ligand is axially symmetric, so the Hamiltonian of an ion in the field of the v-th ligand is written as follows (the quantization axis is directed along the radius-vector \mathbf{R}_{v} of the ligand, the origin placed on the R ion):

$$\mathcal{H}^{(\nu)} = \widetilde{A}_2(R_{\nu}) O_2^0 + \widetilde{A}_4(R_{\nu}) O_4^0 + \widetilde{A}_6(R_{\nu}) O_6^0, \tag{34}$$

where $\tilde{A}_p(R_v)$ are basic ("intrinsic") parameters of the model. Transformation to a local coordinate system used for writing the operator (5) results in:

$$B_{pq} = \sum_{\nu} \widetilde{A}_{p}(R_{\nu}) \kappa_{pq}(\theta_{\nu}, \phi_{\nu})$$
(35)

where the coordination factors depending on angular variables θ_v , ϕ_v of ligands are equal to (numerical factors a_{pq} are given below in table 4)

$$\kappa_{pq} = \begin{cases} a_{pq} O_p^0(\theta_v \phi_v) & q = 0, \\ \frac{1}{2} \frac{a_{pq}}{a_{p0}} O_p^q(\theta_v \phi_v) & q \neq 0. \end{cases}$$
(36)

Three additional parameters t_p are introduced to determine the dependence of "intrinsic" parameters on the distance R between the R ion and the ligand:

$$\widetilde{A}_p(R) = \left(\frac{R_0}{R}\right)^{t_p} \widetilde{A}_p(R_0).$$
(37)

Thus in the superposition model six parameters are used for describing a certain type of the ligand field in a particular lattice. If the sum (5) is restricted to the nearest neighbours of the R ion, artificial overestimation of the short-range interaction occurs. Disregard of the electrostatic component of the crystal field brings about inadequate results when estimating parameters B_{2q} of the crystal field quadrupole components and the parameters of electron-phonon interaction (Newman 1978).

Within the framework of the angular overlap model introduced in its simplest form by Jørgensen et al. (1963), the same approximations as in the superposition model are used. However, energies of the 4f electron (in the axial field of a ligand) with different projections of its orbital moment on the bond direction, serve in this case as "intrinsic" parameters (e_s and e_σ at m=0, e_π at $m=\pm 1$, e_δ at $m=\pm 2$, etc.), and these energies are assumed to be proportional to squares of overlap integrals of the R ion wave functions $|4fm\rangle$ and wave functions of ligand electrons on the outer filled shells. The use of this approximation makes it possible to avoid introducing additional phenomenological parameters which determine the dependence of single-electron energies on the bond length R.

An angular overlap model, modified by taking into account the electrostatic interactions of 4f electron with point multipole moments of lattice ions, has been introduced as the "exchange charge model" by Malkin et al. (1970). This model was also used by Garcia and Faucher (1983), and a more complicated limited LCAO "covalo-electrostatic model" was developed by the same authors (Garcia and Faucher 1985, 1995). The least labourconsuming method of calculating crystal field parameters, which also makes it possible to estimate parameters of electron-phonon interaction in lanthanide crystals with a given spatial structure, is provided by the exchange charge model, and we shall present the corresponding expressions of crystal field parameters in an explicit form below.

By separating out energies of 4f electrons in the fields of point multipoles of the ions constituting the lattice, crystal field parameters may be written as follows:

$$B_{pq} = \sum_{l} B_{pq}^{(l)} + B_{pq}(s).$$
(38)

Index l denotes the rank of a multipole. Parameters of the electrostatic field of point charges (l=0) are presented as

$$B_{pq}^{(0)} = -K_{pq}(1 - \sigma_p) e^2 \langle r^p \rangle \sum_{M\lambda} q_\lambda \left[X \begin{pmatrix} \lambda \\ M \end{pmatrix} \right]^{-p-1} O_p^q(\theta_{M\lambda}, \phi_{M\lambda}), \tag{39}$$

where $X\begin{pmatrix}\lambda\\M\end{pmatrix}$, $\theta_{M\lambda}$ and $\phi_{M\lambda}$ are spherical coordinates of the ion (λ, M) in a coordinate system centered on the R ion, $K_{pq} = \frac{1}{2}a_{pq}^2(q \neq 0), K_{p0} = a_{p0}^2$, and

$$\langle r^{p} \rangle = \int_{0}^{\infty} \left| R_{\rm 4f}(r) \right|^{2} r^{p+2} \,\mathrm{d}r,\tag{40}$$

and σ_p are the shielding constants calculated by Sternheimer et al. (1968) and Erdos and Kang (1972), which take into account linear screening of 4f electrons by outer 5s², 5p⁶-electron shells.

The field parameters for multipoles with l > 0 can be expressed in the derivatives of the point-charge field parameters along ionic coordinates. In particular, parameters of point dipole field are equal to (see also Morrison 1976, Faucher and Garcia 1982, Eremin 1989):

$$B_{pq}^{(1)} = (p+1)K_{pq}\frac{a_{p+1,0}}{a_{p,0}}(1-\sigma_p)e\left\langle r^p\right\rangle \sum_{M\lambda\alpha}\frac{p_{\lambda\alpha}W_{p,\alpha}^q(\theta_{M\lambda}\phi_{M\lambda})}{\left[X\begin{pmatrix}\lambda\\M\end{pmatrix}\right]^{p+2}},\tag{41}$$

where p_{λ} are the dipole moments of the ions of sublattice λ ; $W_{p,\alpha}^q$ are uniform spherical polynomials of the (p+1)-th power, defined by

$$W_{p,\alpha}^{q} \frac{a_{p+1,0}}{a_{p,0}} \frac{p+1}{X^{p+2}} = -\frac{\partial}{\partial X_{\alpha}} \left(\frac{O_{p}^{q}}{X^{p+1}} \right).$$

$$\tag{42}$$

Polynomials $W_{p,\alpha}^q$ are linear combinations of polynomials O_{p+1}^q :

$$b_{pq}W_{p,x}^{q} = \frac{1}{2}\operatorname{sign} q (b_{p+1,q+1} O_{p+1}^{q+1} - b_{p+1,q-1} O_{p+1}^{q+1}), \qquad |q + \frac{1}{2}| \ge \frac{3}{2},$$

$$b_{pq}W_{p,y}^{q} = \frac{1}{2}\operatorname{sign} q (b_{p+1,-q+1} O_{p+1}^{-q+1} + b_{p+1,-q-1} O_{p+1}^{-q-1}), \qquad |q - \frac{1}{2}| \ge \frac{3}{2},$$

$$b_{p0}W_{p,x}^{0} = b_{p+1,1} O_{p+1}^{1}, \qquad b_{p0}W_{p,y}^{0} = b_{p+1,-1} O_{p+1}^{-1},$$

$$b_{pq}W_{p,x}^{q} = b_{p+1,q} O_{p+1}^{q}, \qquad b_{p,-1}W_{p,x}^{-1} = b_{p,1}W_{p,y}^{1} = \frac{1}{2}b_{p+1,-2} O_{p+1}^{-2}.$$
(43)

The factors b_{pq} are given in table 4. By using eq. (43) it is easy to obtain expressions for field parameters of quadrupoles and multipoles of higher ranks similar to eq. (41).

The lattice sums in parameters $B_{pq}^{(l)}$ absolutely converge and may be calculated by direct summation. Special care is needed only when calculating conditionally convergent sums in parameters of quadrupole components $B_{2q}^{(0)}$ of the point charge field, which are proportional to the parameters $Q_{\alpha\beta}(\lambda\lambda')$ of the Lorentz field:

$$B_{2q}^{(0)} = -(1 - \sigma_2) e^2 \langle r^2 \rangle \sum_{\lambda} q_{\lambda} Q_q(0\lambda),$$

$$Q_0 = \frac{1}{4} Q_{zz}, \qquad Q_1 = Q_{xz}, \qquad Q_{-1} = Q_{zy},$$

$$Q_2 = \frac{1}{4} (Q_{xx} - Q_{yy}), \qquad Q_{-2} = \frac{1}{2} Q_{xy}.$$
(44)

In this case correct results may be obtained only by using the Ewald method which makes it possible to estimate an error when taking into account the finite number of terms in sums over direct and reciprocal lattices (Born and Huang 1954):

$$Q_{\alpha\beta}(\lambda\lambda') = \frac{4C^3}{3\sqrt{\pi}} \delta_{\alpha\beta} \delta_{\lambda\lambda'} + \frac{2}{\sqrt{\pi}} C^3 \sum_{L} 'x^{-2} \left[2x_{\alpha} x_{\beta} e^{-x^2} + \left(3\frac{x_{\alpha} x_{\beta}}{x^2} - \delta_{\alpha\beta} \right) \right] \Phi(x) - \frac{4\pi}{\nu} \sum_{h \neq 0} y_{\alpha}(h) y_{\beta}(h) G(h) \cos \left[2\pi y(h) \cdot X \begin{pmatrix} \lambda & \lambda' \\ 0 & 0 \end{pmatrix} \right].$$
(45)

Here C is an arbitrary constant (usually it is appropriate to choose $C \approx (\sqrt{\pi})/v^{1/3}$), the y(h) are reciprocal lattice vectors, and $x = CX\begin{pmatrix} \lambda & \lambda' \\ 0 & L \end{pmatrix}$;

$$G(h) = y^{-2}(h) \exp\left[-\frac{\pi^2 y^2(h)}{C^2}\right],$$
(46)

$$\Phi(x) = e^{-x^2} + \frac{1}{x} \int_x^\infty e^{-t^2} dt.$$
(47)

The prime on the sum over L in eq. (45) indicates the omission of the term with x=0 arising at $\lambda = \lambda'$.
pq	a _{pq}	b _{pq}	pq	a _{pq}	b_{pq}	pq	a _{pq}	b _{pq}
00	1	1	50	<u> </u> 8	1	72	$\frac{\sqrt{21}}{16}$	3
10	1	1	51	$\frac{\sqrt{30}}{8}$	3	73	$\frac{\sqrt{42}}{32}$	3
11	$\sqrt{2}$	1	52	$\frac{\sqrt{210}}{4}$	21	74	$\frac{\sqrt{462}}{16}$	33
20	$\frac{1}{2}$	1	53	$\frac{\sqrt{35}}{8}$	7	75	$\frac{\sqrt{462}}{32}$	33
21	$\sqrt{6}$	3	54	$\frac{\sqrt{630}}{8}$	63	76	$\frac{\sqrt{3003}}{16}$	429
22	$\frac{\sqrt{6}}{2}$	3	55	$\frac{\sqrt{63}}{8}$	63	77	$\frac{\sqrt{858}}{32}$	429
30	$\frac{1}{2}$	1	60	$\frac{1}{16}$	1	80	$\frac{1}{128}$	1
31	$\frac{\sqrt{3}}{2}$	1	61	$\frac{\sqrt{42}}{8}$	7	81	$\frac{\sqrt{2}}{32}$	3
32	$\frac{\sqrt{30}}{2}$	5	62	$\frac{\sqrt{105}}{16}$	7	82	$\frac{\sqrt{315}}{32}$	45
33	$\frac{\sqrt{5}}{2}$	5	63	$\frac{\sqrt{105}}{8}$	21	83	$\frac{\sqrt{2310}}{32}$	165
40	<u>1</u> 8	1	64	$\frac{\sqrt{126}}{16}$	21	84	$\frac{\sqrt{1386}}{64}$	99
41	$\frac{\sqrt{5}}{2}$	5	65	$\frac{\sqrt{693}}{8}$	231	85	$\frac{\sqrt{18018}}{32}$	1287
42	$\frac{\sqrt{40}}{8}$	5	66	$\frac{\sqrt{231}}{16}$	231	86	$\frac{\sqrt{429}}{32}$	429
43	$\frac{\sqrt{35}}{2}$	35	70	<u>1</u> 16	1	87	$\frac{\sqrt{12870}}{32}$	6435
44	$\frac{\sqrt{70}}{8}$	35	71	$\frac{\sqrt{14}}{32}$	1	88	$\frac{\sqrt{12870}}{128}$	6435

 Table 4

 Proportionality factors between spherical operators and uniform spherical polynomials

The main problem when estimating the point multipole field parameters lies in the correct determination of multipole moments of ions. Ionic charge density distribution in a crystal lattice is governed not only by the self-consistent inhomogeneous internal electric field (Faucher and Garcia 1982) but also by redistribution of electron density due to overlapping of wave functions of neighbouring ions (Bogomolova et al. 1977, Satoh and Taki 1981). Owing to the significant difference of multipole polarizabilities of free ions and ions in a crystal (Sen and Narasinahan 1977, Schmidt et al. 1979) it is advisable to consider tensor polarizabilities of ions as fitting parameters if necessary information about the Stark structure of the R ion spectrum is available.

Corrections to the Coulomb interaction due to the spatial distribution of ligand charge, contributions to 4f-electron energy from states with charge transfer from ligands to the R ion, and contributions of exchange interactions in the exchange charge model are parametrized by introducing the field of fictituous positive charges which are proportional to squares of overlap integrals of 4f-electron wave functions and electronic wave functions of ligands (the second term in eq. 38). Parameters of the exchange charge field corresponding to ligands with the outer $n''s^2$ and $n''p^6$ electron shells are equal to (Malkin 1987)

$$B_{pq}(s) = \frac{2(2p+1)}{7} K_{pq} e^2 \sum_{\nu} S_p(R_{\nu}) \frac{O_p^q(\theta_{\nu}\phi_{\nu})}{R_{\nu}},$$
(48)

where S_p are quadratic forms of the overlap integrals:

$$S_{p} = G_{s} |S_{s}|^{2} + G_{\sigma} |S_{\sigma}|^{2} + G_{\pi} \gamma_{p} |S_{\pi}|^{2},$$

$$S_{s} = \langle 430 | n''00 \rangle, \qquad S_{\sigma} = \langle 430 | n''10 \rangle, \qquad S_{\pi} = \langle 43, \pm 1 | n''1, \pm 1 \rangle,$$
(49)

and G_s , G_{σ} , G_{π} are dimensionless parameters of the model; the numerical factors γ_p for f electrons are equal to zero if p = 1, 3, 5; $\gamma_2 = \frac{3}{2}$, $\gamma_4 = \frac{1}{3}$, $\gamma_6 = -\frac{3}{2}$.

Actually, the described model is based on an assumption that the energy of the valence electron, defined by overlapping of its wave function φ with the wave function ψ_v of the electron localized on the ligand v, is proportional to the value of an exchange charge with spatial density $2e\varphi\psi_v^*S_v$, where $S_v = \langle \varphi | \psi_v \rangle$ (Dick and Overhauser 1958). An analysis of the ligand field based on an approximation of Wolfsberg and Helmholz (1952) has first been carried out by Axe and Burns (1966) for Tm²⁺ ion in a fluorite. Their calculations showed that different types of bonds play comparable roles in forming the Stark structure of the R ion spectrum. Thus it is possible to restrict the simplest exchange charge model to a single phenomenological parameter $G = G_s = G_{\sigma} = G_{\pi}$.

2.3. Stark spectrum of a lanthanide ion in a static lattice

Total splittings of the R ion multiplets in crystals are of the order of 100–1000 K, and for treatment of magnetic properties of the lanthanide compounds at all temperatures of interest, analysis of the Stark structure of a ground multiplet without its admixture

Table	5
Table	2

Calculated and measured (in brackets) energies of the ground multiplet sublevels of lanthanide ions in crystals

Compound	$\varepsilon(\Gamma_i)$ (cm ⁻¹)	References
Van Vleck para	magnets	
LiTmF ₄	0 (Γ_2), 31.1 (31 Γ_1), 60.6 (56 $\Gamma_{3,4}$), 294.4 (282 Γ_2), 322 (319 Γ_2), 371.8 (363 $\Gamma_{3,4}$), 384.6 $\Gamma_{3,4}$, 412.9 $\Gamma_{3,4}$, 426 Γ_1 437.7 Γ_2	Christensen (1979b), , Kupchikov et al. (1982)
TmES	0 (Γ_1), 31.7 (32.1 Γ_5), 111.5 (110.9 Γ_6), 159.2 (157.3 Γ_3), 199.7 Γ_5 , 214.2 Γ_2 , 220.7 Γ_1 , 277 Γ_6 , 304.1 Γ_4	Barnes et al. (1964)
TmPO₄	0 (Γ_1), 26.9 (29 Γ_5), 71.9 (78.2 Γ_4), 130.3 (136.3 Γ_5), 180 (184.7 Γ_2), 242.7 (255 Γ_1), 277.1 Γ_3 , 279 (280.7 Γ_5), 355.5 (338 Γ_4), 359.5 (338 Γ_3)	Loong et al. (1993a)
TmBa ₂ Cu ₃ O ₆	0 Γ_4 , 127 Γ_5 , 174 Γ_3 , 218 Γ_1 , 259 Γ_4 , 675 Γ_2 , 678 Γ_5 , 715 Γ_2 726 Γ_3 , 740 Γ_1	5, Bakharev et al. (1992b)
TmBa ₂ Cu ₃ O _{6.5}	0 Γ_3 , 115 Γ_4 , 127 Γ_2 , 192 Γ_1 , 210 Γ_1 , 275 Γ_3 , 662 Γ_2 , 678 Γ_3 695 Γ_4 , 714 Γ_4 , 715 Γ_1 , 722 Γ_2 , 749 Γ_1	Bakharev et al. (1992b)
TmBa ₂ Cu ₃ O ₇	0 Γ_3 , 106 Γ_4 , 127 Γ_2 , 204 Γ_1 , 209 Γ_1 , 288 Γ_3 , 650 Γ_2 , 682 Γ_2 704 Γ_1 , 712 Γ_4 , 715 Γ_4 , 731 Γ_2 , 761 Γ_1	, Bakharev et al. (1992b)
TmBa ₂ Cu ₄ O ₈	0 (Γ_3), 103 (103 Γ_4), 130 (114 Γ_2), 209 (210 Γ_1), 210 (210 Γ_1), 288 Γ_3 , 639 Γ_2 , 654 Γ_3 , 682 Γ_4 , 693 Γ_1 , 698 Γ_4 , 707 Γ_2 , 741 (742 Γ_1)	Ishigaki et al. (1995)
HoVO₄	0 (Γ_1), 21.4 (20.7 Γ_5), 48.2 (46.5 Γ_3), 48.5 (46.5 Γ_5), 120 (116.6 Γ_4), 131 (132 Γ_3), 222.3 Γ_4 , 225.4 (236.2 Γ_5), 229.2 Γ_2 , 229.5 Γ_1 , 260.2 Γ_5 , 262.5 (275.2 Γ_2), 292 Γ_1	Enderle et al. (1990a), Bleaney et al. (1988b)
Cs₂NaHoCl ₆	0 (Γ_3), 8.3 (10.1 Γ_4), 29 (48 Γ_1), 216.6 (200 Γ_4), 245.6 (242 Γ_5), 288 (288 Γ_3), 289 (288 Γ_5)	Richardson et al. (1985), Kostetskii (1988)
HoBa ₂ Cu ₃ O ₇	0 (Γ_3), 4.4 (4 Γ_2), 14.8 (14.5 Γ_4), 30 (30.5 Γ_1), 35 (35 Γ_3), 66 (65 Γ_1), 87 (87 Γ_4), 91 (93 Γ_2), 459 Γ_3 , 465 Γ_1 , 477 (474 Γ_3), 478 (474 Γ_2), 480 Γ_4 , 501 Γ_1 , 561 (562 Γ_4), 565 Γ_2 , 586 (586 Γ_1)	Furrer et al. (1988)
Ferromagnets a	nd antiferromagnets	
Kramers double	t as a ground state	
DyES	0 ($\Gamma_{9,10}$), 16 ($\Gamma_{11,12}$), 20.2 ($\Gamma_{7,8}$), 59.3 ($\Gamma_{9,10}$), 68.3 ($\Gamma_{7,8}$), 148.7 ($\Gamma_{11,12}$), 201.5 $\Gamma_{9,10}$, 241.8 $\Gamma_{7,8}$	Powell and Orbach (1961)
LiDyF₄	0 ($\Gamma_{5,6}$), 16.6 (14.2 $\Gamma_{7,8}$), 40.5 (41.1 $\Gamma_{7,8}$), 65 (62 $\Gamma_{7,8}$), 74.7 (70.2 $\Gamma_{5,6}$), 117.6 $\Gamma_{5,6}$, 359 $\Gamma_{5,6}$, 371.4 $\Gamma_{7,8}$	Davidova et al. (1977)
$DyBa_2Cu_3O_7$	0 (Γ_5), 27 (27 Γ_5), 48 (47 Γ_5), 111 (111 Γ_5), 129 (135 Γ_5), 294 Γ_5 , 421 Γ_5 , 433 Γ_5	Allenspach et al. (1989)
LiErF₄	0 ($\Gamma_{7,8}$), 16.5 (18.2 $\Gamma_{5,6}$), 22.3 (23.3 $\Gamma_{7,8}$), 57.2 (60 $\Gamma_{5,6}$), 245.5 $\Gamma_{5,6}$, 289.1 $\Gamma_{5,6}$, 316.7 $\Gamma_{7,8}$, 343.9 $\Gamma_{7,8}$	Christensen (1979a)
ErBa ₂ Cu ₃ O ₇	0 (Γ_5), 74 (74 Γ_5), 79 (79 Γ_5), 87 (88 Γ_5), 552 (546 Γ_5), 584 (582 Γ_5), 616 (618 Γ_5), 646 (650 Γ_5)	Podlesnyak et al. (1991)
YbBa ₂ Cu ₃ O ₇	0 (Γ_5), 714 (711 Γ_5), 748 (745 Γ_5), 794 (791 Γ_5)	Guillaume et al. (1992) continued on next page

Compound	$\varepsilon(\Gamma_i)$ (cm ⁻¹)	References
non-Kramers do	ublet as a ground state	
LiHoF ₄	0 ($\Gamma_{3,4}$), 6.2 (8 Γ_2), 19.9 (26 Γ_2), 46.2 (49 Γ_1), 54.7 (61 Γ_1), 67.4 (78 $\Gamma_{3,4}$), 200.5 Γ_1 , 253.1 $\Gamma_{3,4}$, 256 Γ_1 , 261.8 Γ_2 , 275.3 Γ_1 , 277.7 $\Gamma_{3,4}$, 291.7 Γ_2	Christensen (1979a)
HoES	0 (Γ_5), 3.5 (6 Γ_1), 38 (47 Γ_2), 73.2 (74 Γ_5), 99 (101 Γ_6), 112.8 (117 Γ_3), 156.9 Γ_1 , 189.8 Γ_5 , 204.2 Γ_6 , 240.6 Γ_6 , 256.9 Γ_4	Grohmann et al. (1961)
HoPO ₄	0 (Γ_5), 68.1 (66.1 Γ_3), 71.5 (71.7 Γ_1), 80.2 (80.7 Γ_4), 90.4 (94 Γ_5), 158.9 (162.1 Γ_3), 183.1 (184.3 Γ_2), 184.6 (184.3 Γ_1), 222.2 Γ_5 , 238.4 (244.4 Γ_4), 268.8 Γ_5 , 272.2 (279.3 Γ_2), 291.9 Γ_1	Loong et al. (1993c)
HoAsO ₄	0 (Γ_5), 6.1 (7.7 Γ_1), 26.6 (27.8 Γ_5), 31.9 (29.5 Γ_3), 57.8 (59.5 Γ_4), 100.1 (108.9 Γ_3), 171.2 (182.1 Γ_5), 176.5 (190.3 Γ_4), 181.9 Γ_2 , 185.5 Γ_1 , 205.8 (220.2 Γ_5), 214.3 Γ_2 , 232.7 (229.3 Γ_1)	Enderle et al. (1990b)
Quasidoublet as	a ground state	
TbES	0 (Γ_1), 0.445 (0.4 Γ_2), 102.2 (101.4 Γ_5), 111.9 Γ_1 , 128.8 Γ_5 , 149 Γ_6 , 167.5 Γ_3 , 178.1 Γ_6 , 195 Γ_4	Larson and Jeffries (1966a)
LiTbF ₄	0 (Γ_2), 1.05 (1 Γ_2), 108.3 (107 $\Gamma_{3,4}$), 117 (124 Γ_1), 133 (136 Γ_2), 174.5 (166 $\Gamma_{3,4}$), 233 (217 Γ_1), 375 Γ_1 , 390 $\Gamma_{3,4}$, 402 Γ_2	Christensen (1978)
Crystals under	going Jahn–Teller transitions	
$TbVO_4 T > T_D$	0 (Γ_1), 9.7 (8.6 Γ_5), 22.4 (22.9 Γ_4), 80.9 Γ_2 , 87.8 (91.5 Γ_5), 161.6 Γ_3 , 176 Γ_1 , 182 Γ_5 , 205 Γ_4 , 218 Γ_3	Elliott et al. (1972)
$T < T_{\rm D}$	0, 0.9, 47.9, 51.3, 90.2, 93.9,	
$TbAsO_4$ $T > T_D$	0 (Γ_1), 6.2 (5.8 Γ_5), 15.4 (15.3 Γ_4), 87 (87.8 Γ_5), 89.7 Γ_2 , 130.5 Γ_3 , 147.9 Γ_4 , 165.3 Γ_1 , 169.4 Γ_5 , 180.1 Γ_3	Muller et al. (1983)
$T < T_{\rm D}$	0, 0.6, 38.6, 41.7	
$TbPO_4$ $T > T_D$	0 (Γ_5), 2 (2.5 Γ_4), 10.5 (9.5 Γ_3), 25 (20.7 Γ_1), 95.6 (74 Γ_2), 96.6 (85 Γ_5), 101.8 (92 Γ_4), 249.7 (241 Γ_1), 259.6 (254 Γ_5), 268.6 (262 Γ_3)	Sen et al. (1988), Loong et al. (1993b)
$TmVO_4$ $T > T_D$	0 (Γ_5), 38.9 (54 Γ_1), 108.8 (119 Γ_4), 134.5 (138 Γ_5),134.8 Γ_2 , 154.6 (158 Γ_3), 186.7 (192 Γ_4), 278.4 Γ_1 , 315.1 (335 Γ_5), 340.7 (361 Γ_3)	Knoll (1971)
$TmAsO_4$ $T > T_D$	0 (Γ_5), 14.2 (13.7 Γ_1), 87.2 (72.4 Γ_4), 88.4 (98.7 Γ_5), 139.2 (Γ_2), 169.4 (Γ_3), 175.1 (Γ_4), 224.4 (Γ_1), 279.8 (Γ_5), 299.7 (Γ_3)	Bingham et al. (1984a)
$DyVO_4 T > T_D$	0 ($\Gamma_{8,9}$), 5.9 (9 $\Gamma_{6,7}$), 137.2 (125 $\Gamma_{6,7}$), 157.7 ($\Gamma_{6,7}$), 186.9 ($\Gamma_{8,9}$), 260.7 ($\Gamma_{8,9}$), 272.6 ($\Gamma_{6,7}$), 288.3 ($\Gamma_{8,9}$)	Elliott et al. (1972)
$T < T_{\rm D}$	0, 27.5	

Table 5, continued

Table 6 General structure of the wave functions $\psi(\Gamma_i)$ corresponding to the irreducible representations Γ_i of the point symmetry group G of the R sites

G	Wave functions $\psi(\Gamma_i)$
C _{3h}	$\psi(\Gamma_1) = \alpha(6\rangle + -6\rangle) + \beta 0\rangle$
	$\psi(\Gamma_2) = \alpha(6\rangle - -6\rangle)$
	$\psi(\Gamma_3) = \alpha(3\rangle + -3\rangle)$
	$\psi(\Gamma_4) = \alpha(3\rangle - -3\rangle)$
	$\psi(\Gamma_5) = \alpha \pm 5\rangle + \beta \mp 1\rangle$
	$\psi(\Gamma_6) = \alpha \pm 4\rangle + \beta \mp 2\rangle$
	$\psi(\Gamma_{7,8}) = \alpha \pm 13/2\rangle + \beta \pm 1/2\rangle + \gamma \mp 11/2\rangle$
	$\psi(\Gamma_{9,10}) = \alpha \pm 15/2\rangle + \beta \pm 3/2\rangle + \gamma \mp 9/2\rangle$
	$\psi(\Gamma_{11,12}) = \alpha \pm 7/2\rangle + \beta \mp 5/2\rangle$
D _{2h}	$\psi(\Gamma_1) = \alpha(8\rangle + -8\rangle) + \beta(6\rangle + -6\rangle) + \gamma(4\rangle + -4\rangle) + \delta(2\rangle + -2\rangle) + \eta 0\rangle$
	$\psi(\Gamma_2) = \alpha(7\rangle - -7\rangle) + \beta(5\rangle - -5\rangle) + \gamma(3\rangle - -3\rangle) + \delta(1\rangle - -1\rangle >)$
	$\psi(\Gamma_3) = \alpha(8\rangle - -8\rangle) + \beta(6\rangle - -6\rangle) + \gamma(4\rangle - -4\rangle) + \delta(2\rangle - -2\rangle)$
	$\psi(\Gamma_4) = (7\rangle + -7\rangle) + \beta(5\rangle + -5\rangle) + \gamma(3\rangle + -3\rangle) + \delta(1\rangle + -1\rangle)$
	$\psi(\Gamma_5) = \alpha \pm 15/2\rangle + \beta \pm 11/2\rangle + \gamma \pm 7/2\rangle + \delta \pm 3/2\rangle + \eta \mp 1/2\rangle + \lambda \mp 5/2\rangle + \mu \mp 9/2\rangle + \nu \mp 13/2\rangle$
D _{2d} ,	$\psi(\Gamma_1) = \alpha(8\rangle + -8\rangle) + \beta(4\rangle + -4\rangle) + \gamma 0\rangle$
D _{4h}	$\psi(\Gamma_2) = \alpha(8\rangle - -8\rangle) + \beta(4\rangle - -4\rangle)$
	$\psi(\Gamma_3) = \alpha(6\rangle + -6\rangle) + \beta(2\rangle + -2\rangle)$
	$\psi(\Gamma_4) = \alpha(6\rangle - -6\rangle) + \beta(2\rangle - -2\rangle)$
	$\psi(\Gamma_5) = \alpha \pm 7\rangle + \beta \pm 3\rangle + \gamma \mp 1\rangle + \delta \mp 5\rangle$
	$\psi(\Gamma_{6,7}) = \alpha \pm 15/2\rangle + \beta \pm 7/2\rangle + \gamma \mp 1/2\rangle + \delta \mp 9/2\rangle$
	$\psi(\Gamma_{8,9}) = \alpha \pm 13/2\rangle + \beta \pm 5/2\rangle + \gamma \mp 3/2\rangle + \delta \mp 11/2\rangle$
S ₄	$\psi(\Gamma_1) = \alpha 8\rangle + \beta -8\rangle + \gamma 4\rangle + \delta -4\rangle + \varepsilon 0\rangle$
	$\psi(\Gamma_2) = \alpha 6\rangle + \beta -6\rangle + \gamma 2\rangle + \delta -2\rangle$
	$\psi(\Gamma_{3,4}) = \alpha \pm 7\rangle + \beta \pm 3\rangle + \gamma \mp 1\rangle + \delta \mp 5\rangle$
	$\psi(\Gamma_{5,6}) = \alpha \pm 15/2\rangle + \beta \pm 7/2\rangle + \gamma \mp 1/2\rangle + \delta \mp 9/2\rangle$
	$\psi(\Gamma_{7,8}) = \alpha \pm 13/2\rangle + \beta \pm 5/2\rangle + \gamma \mp 3/2\rangle + \delta \mp 11/2\rangle$
	continued on next page

with excited multiplets is quite sufficient. Cooperative effects due to interactions between R ions, which lead to a spontaneous break of crystal symmetry, are realized at temperatures of the order of 10 K and lower, when only the lowest sublevels of a ground multiplet are markedly populated.

The multiplet splitting is qualitatively determined by the point symmetry of a crystal field acting on an R ion, and the numerical characteristics of the Stark spectrum may be

	Tabl	le	6,	continued
--	------	----	----	-----------

G	Wave functions $\psi(\Gamma_i)$
O _h	$\psi(\Gamma_1) = \alpha(8\rangle + -8\rangle) + \beta(4\rangle + -4\rangle) + \gamma 0\rangle$
	$\psi_1(\Gamma_3) = \alpha(6\rangle + -6\rangle) + \beta(2\rangle + -2\rangle)$
	$\psi_2(\Gamma_3) = \alpha(8\rangle + -8\rangle) + \beta(4\rangle + -4\rangle) + \gamma 0\rangle$
	$\psi_1(\Gamma_4) = \alpha(8\rangle - -8\rangle) + \beta(4\rangle - -4\rangle)$
	$\psi_{2,3}(\Gamma_4) = \alpha \pm 7\rangle + \beta \pm 3\rangle + \gamma \mp 1\rangle + \delta \mp 5\rangle$
	$\psi_1(\Gamma_5) = \alpha(6\rangle - -6\rangle) + \beta(2\rangle - -2\rangle)$
	$\psi_{2,3}(\Gamma_5) = \pm 7\rangle + \beta \pm 3\rangle + \gamma \mp 1\rangle + \delta \mp 5\rangle$

obtained from optical measurements (absorption and luminescence spectra, resonant and nonresonant electronic Raman scattering), from the temperature dependence of magnetic susceptibility and investigations of inelastic neutron scattering (see, e.g., Christensen 1979a,b, Beauvillain et al. 1980b, Loong et al. 1993a-c, Kupchikov et al. 1982).

Energy levels of ions with an odd number of electrons on the 4f-shell are Kramers doublets, a possible exception is the case of a cubic symmetry when four-fold degeneracy of an energy level is feasible.

If the ground state of an ion with an even number of 4f electrons (non-Kramers ion) is a singlet or non-magnetic doublet (g-factor equals zero; this case might occur in a crystal field of cubic symmetry), then at low temperatures and usual magnetic fields $(\Delta \gg k_B T, g_I \mu_B H)$, where Δ is the energy of the nearest excited sublevel) a corresponding compound has only the Van Vleck magnetic moment. When two neighbouring singlets (or a singlet and a doublet) are mixed by a Zeeman energy operator and the corresponding matrix elements of \mathcal{H}_Z are comparable or exceed the energy difference, Δ , of these states, it is possible to consider quasidoublet (quasitriplet) states. In an axial field a non-Kramers ion spectrum may contain doublets along with singlets.

The measured energies (along with the calculated ones) of an R ion ground multiplet sublevels, for compounds whose properties are discussed in greater detail in subsequent sections of the present chapter, are given in table 5. As a rule, multiplet splittings in magnetically concentrated crystals and isostructural diamagnetic compounds of La, Y, and Lu, doped with the corresponding R ions, differ insignificantly (alterations of intervals between neighbouring sublevels do not exceed 10 cm^{-1} which correlates with the upper estimate of the 4f-zone width in concentrated lanthanide magnets). The data in table 5 are in part deduced from the optical spectra of diluted compounds, which are much simpler to interpret due to the smaller width of spectral lines. The symmetry properties of eigenfunctions for energy levels in table 5 are specified by symbols Γ_i (in notation of Bethe 1929) of the irreducible representations of the rare-earth site symmetry group G. The general structure of wavefunctions $\psi(\Gamma_i)$ for different groups and values of J is given in table 6.

RMO₄	B_{20}	B_{40}	B ₆₀	B ₄₄	B ₆₄	References
TbVO₄	-68	51	-50	750	-30	Andronenko and Bazhan (1989)
HoVO₄	-96.2	43	-45.8	836	-83.4	Bleaney et al. (1988b)
TmVO₄	-107	37.5	-34.5	750	-17	Vinokurov et al. (1988b)
TmVO ₄ (theory)	-93	34	-36	903	-81	Pekurovskii and Andronenko (1984)
TbAsO₄	-41.4	17	-40.7	708	24.4	Muller et al. (1983)
TbAsO₄	-20.5	7.1	-41.4	693	13.3	Bischoff et al. (1991)
TmAsO ₄	-37	15.7	-42	680	60	Hodges (1983b)
TmAsO ₄ (theory)	-39	32	-36	791		Pekurovskii and Andronenko (1984)
TbPO₄	176	14	-50	887	-106	Bohm et al. (1984)
HoPO₄	187	7.5	-45.4	692	40	Loong et al. (1993c)
TmPO₄	158	27.6	-44	697	51.8	Loong et al. (1993a)
TmPO₄ (theory)	185	32	-32.2	778	2.0	Pekurovskii and Andronenko (1984)

Table 7a Crystal field parameters (in cm^{-1}) in crystallographic axes, RMO, compounds

As can be seen from table 5, the measured structures of ground multiplets are well described by empirical crystal field parameters (given in tables 7a–d), found by an analysis of splittings of excited multiplets. In some cases (e.g., in a TmVO₄ crystal) the essential difference in calculated energies and their measured values indicates the necessity to define more accurately the nature of the corresponding spectral line. A comparison of crystal field parameters given in tables 7a–d for different crystals shows that the most essential parameters B_{pq} change monotonously in isostructural compounds – they increase with the growth of the 4f-shell radius when the nuclear charge decreases and are weakly dependent on the bond ionicity.

Comparison of the empirical parameters with those calculated within the framework of the exchange charge model (results in tables 7a–d, "theory" rows), shows that correlations between values of B_{pq} are mainly determined by the spatial structure of the lattice; these values may be found by determining the scale factors G_{σ} , G_s , G_{π} (see eq. 49) and effective ionic charges q_{λ} from comparison of the calculation results with the data of measurements.

Although the fitted G_{γ} values of the model phenomenological parameters are dependent on the electronic radial wave functions of R ions and ligands, used in the computations, the calculated values of crystal field parameters depend weakly on specific values of overlap integrals and moments $\langle r^{\rho} \rangle$ of 4f-shell charge density distribution (see Freeman and Watson 1962, Freeman and Desclaux 1979). Overlap integrals of Nd³⁺, Eu³⁺ and Tm³⁺ ions with O²⁻, Cl⁻ and F⁻ ligands as functions of interionic distance are given by Garcia and Faucher (1985), and by Davidova et al. (1978) for different R ions in fluorine surroundings.

NONMETALLIC LANTHANIDE COMPOUNDS

Crystal field parameters (in cm ⁻¹) in crystallographic axes, RES compounds								
RES	B ₂₀	B ₄₀	B ₆₀	B [*] ₆₆	References			
TbES	110.6	-75	-34	406	Neogy et al. (1978)			
DyES	124	-79	-31	492	Powell and Orbach (1961)			
HoES	126	-81	-31	360	Erath (1961)			
TmES	130.5	-65.9	-28.6	427.3	Barnes et al. (1964)			
TmES (theory) ^a	137.4	-93.3	-28.2	334	This chapter, eqs. (48), (49)			

Table 7b ystal field parameters (in cm⁻¹) in crystallographic axes, RES compour

^a $q_{\lambda} = 0; G = 16.3; B_{66}^* = [(B_{66})^2 + (B_{6-6})^2]^{1/2}.$

Table 7c Crystal field parameters (in cm^{-1}) in crystallographic axes, LiRF₄ compounds

LiRF₄	B ₂₀	B ₄₀	B ₆₀	B ₄₄	B ₄₋₄	B ₆₄	B ₆₋₄	References
LiTbF₄	237	-54.1	4.0	854	-739	-477	-291	Christensen (1978)
LiDyF₄	165	-88	-4.4	-741	-641	-370	-223	Davidova et al. (1977)
LiHoF₄	189.5	-78.2	-3.25	-657	-568	-364	-222	Christensen (1979a)
LiErF₄	190	-80	-2.3	-771	-667	-363	-222	Davidova et al. (1977)
LiTmF₄	184		-4.06	-727	-628.5	-328	-284	Christensen (1979b)
LiTmF ₄ (theory)	176.7	-84.9	-2.76	-699	-604	-332	-253	Bumagina et al. (1981)

Table 7d Crystal field parameters (in cm⁻¹) in crystallographic axes, RBaCuO compounds

R–Ba–Cu–O	B ₂₀	B ₂₂	B ₄₀	B ₄₂	B ₄₄	B ₆₀	B ₆₂	B ₆₄	B ₆₆	References
DyBa ₂ Cu ₃ O ₇	127	39	-191	46	912	15	-3	405	3	Allenspach et al. (1989)
HoBa2Cu3O2	167	72	-220	15	1017	28	-17	841	-12	Furrer et al. (1988)
ErBa ₂ Cu ₃ O _{6.98}	112	94	-260	83	1265	30	-5	844	5	Mesot et al. (1993b)
ErBa ₂ Cu ₃ O ₇ (theory)	200	100	-216	99	733	31	-7	795	14	Avanesov et al. (1994)
ErBa2Cu3O6.09	51	0	-271	0	1261	29	0	843	0	Mesot et al. (1993b)
ErBa ₂ Cu ₃ O ₆ (theory)	151	0	-213	0	708	28	0	752	0	Avanesov et al. (1994)
YbBa ₂ Cu ₃ O ₇	46	16	-261	65	1207	36	5	883	5	Guillaume et al. (1992)
TmBa ₂ Cu ₃ O ₇	76	100	-248	43	1336	30	20	811	-6	Bakharev et al. (1992b)
TmBa ₂ Cu ₃ O _{6.5}	56	56	-250	26	1327	31	10	811	-2	Bakharev et al. (1992b)
TmBa ₂ Cu ₃ O ₆	32	0	-250	0	1335	32	0	807	0	Bakharev et al. (1992b)
$(Y,Tm)Ba_2Cu_4O_8$	65	72	-230	32	1325	29	44	804	-2	Ishigaki et al. (1995)

Crystals containing halogen ions are characterized by a high degree of ionicity. Charges of ions have corresponded to their valencies: -e (F⁻, Cl⁻), +e (Li⁺, K⁺, Cs⁺, Na⁺), +3e (R³⁺) in calculations of the crystal field parameters within the framework of the exchange charge model for lithium–lanthanide double fluorides (Bumagina et al. 1981), trifluorides with the YF₃ structure (Bumagina et al. 1977, Davidova et al. 1978), and cubic elpasolites (Kostetskii 1988). The number of independent components of ion multipole moments is determined by the spatial symmetry of a crystal; in particular, in tetrafluorides LiRF₄ only F⁻ ions are polarized, and dipole moments of eight fluorine sublattices are equal by absolute value ($|p_{\lambda}| = 0.157 e$ Å) and differ in orientation, so that the total polarization of the unit cell equals zero. Absolute values of the quadrupole moment components of fluorine ions do not exceed 0.2 e Å². (The given values of dipole and quadrupole moments of F⁻ ions in LiRF₄ have been found by using scalar polarizabilities $\alpha_p = 0.97$ Å³ and $\alpha_Q = 0.63$ Å⁵ (Schmidt et al. 1979), and they should be considered as the upper limits of the real values.)

Practically in all crystal-field calculations the single-parameter variant of the exchange charge model has been employed with one fitting parameter $G = G_{\sigma} = G_s = G_{\pi}$, using the wave functions of Freeman and Watson (1962). An exchange charge field mainly contributes to the B_{4q} , B_{6q} crystal field parameters. The corresponding contributions of the point charge field do not exceed 10–30%. The multipolar fields principally form only the quadrupole components of a crystal field, determined by parameters B_{2q} . For instance, the terms of the B_{20} parameter in the LiErF₄ crystal ($B_{20}^{(0)} = 42$, $B_{20}^{(1)} = 97$, $B_{20}^{(2)} = 52$, $B_{20}(s) = 37 \text{ cm}^{-1}$) are of the same order of magnitude. The problem of the convergence of multipolar expansion in the calculation of 4f-electron energy in an electrostatic field of an ionic lattice has been discussed repeatedly (Faucher and Garcia 1982, Hutchings 1964); actually the series has been cut off without rigorous reasons and estimation of errors. Nevertheless the correct calculations of several first terms of multipolar expansion are necessary to preserve the main peculiarities of the crystal electrostatic field within the framework of the model considered.

Calculations of the crystal field parameters for lanthanide ions in oxygen surroundings, demand the correct determination of an effective charge of oxygen ions which are often bound in molecular complexes. For compounds with a mixed ionic-covalent type of bonding, the overlap integrals should be calculated by using molecular orbitals of covalent complexes surrounding the R ions; the corresponding algorithm of calculations has been developed by Avanesov et al. (1992). Actually, the formation of the molecular orbitals may be taken into account by variation of the parameters G_{ν} of the exchange charge field (see eq. 49) and ligand polarizabilities. A satisfactory description of the R ion spectra in vanadates, arsenates, phosphates, in which the R ion surroundings consist of six (MO₄)³⁻ complexes (M=V, As, P; each of the two nearest coordination spheres of a rare-earth ion contains four oxygen ions), has been achieved by Pekurovskii and Andronenko (1984) at the fixed charge value +3e of R-ions, neglecting R ion-ligand π -bonds ($G_{\pi} = 0$) and varying the parameters $G_1 = G_{\sigma} = G_s$ and the effective charge q_0 of an oxygen ion. For the description of the different R ion spectra it appeared possible to use the same value of parameter $G_1 = 8$ and the values $q_0 = -e; -1.02 e; -1.05 e$ in phosphates, arsenates, and vanadates, respectively. It should be noted that small changes of structural parameters and effective charges of oxygen ions in the crystal series RVO_4 -RAsO₄-RPO₄ result in significant changes of the long-range electrostatic field of the lattice, characterized by the parameter B_{20} . In the case of lanthanide ethylsulfates R ions are surrounded by nine water molecules, and a satisfactory description of the crystal field is achieved by taking into account only the field of exchange charges located on the R-O bonds (see table 7b).

An analysis of spectral data for tetrafluorides and ethylsulfates gives only six and four parameters instead of seven and five, respectively, since energies of Stark sublevels of R ions in positions with point symmetry S₄ and C_{3h} depend only on $B'_{44} = (B^2_{44} + B^2_{4-4})^{1/2}$ and $B'_{66} = (B^2_{66} + B^2_{6-6})^{1/2}$. The values B_{44} , B_{4-4} , B_{64} , B_{6-4} given in table 7c are obtained from empirical sets of parameters, using the calculated value of the B_{44}/B_{4-4} ratio. For ethylsulfates in the crystallographic coordinate system the calculated value of B_{66}/B_{6-6} ratio equals ~-6.1.

The information on the Stark structure of the lanthanide ion energy spectra in the RBa₂Cu₃O_{6+x} high-T_c superconductors is available from inelastic (magnetic) neutron scattering spectra (see table 5, the wave-functions of the Stark sublevels at the sites with tetragonal D_{4h} (x = 0) and orthorhombic D_{2h} (x = 1) symmetry are given in table 6). The Tm³⁺ ion spectra in the TmBa₂Cu₃O_{6+x} compounds have been obtained from neutron scattering and NMR measurements (see sect. 6). The corresponding crystal field parameters for Tm³⁺, Ho³⁺, Dy³⁺ and Er³⁺ ions derived from the spectroscopic data are given in table 7d. The magnitudes of the basic crystal field parameters (B_{20} , B_{40} , B_{44} , B_{60} and B_{64}) vary monotonously along the lanthanide series. Comparison of the crystal field potentials in the RBa₂Cu₃O₆ and RBa₂Cu₃O₇ crystals with the same rare-earth sublattice shows that the parameters B_{40} , B_{44} , B_{60} and B_{64} do not depend much on the oxygen content (they vary no more than for 4%), but the B_{20} parameter variations exceed 100%. No radical changes occur in the nearest environment of the R ion when oxygen index x decreases from 1 to 0, therefore the values of B_{40} , B_{44} , B_{60} and B_{64} parameters determined mainly by the overlapping of the 4f-electron wave functions with the 2p and 2s electron wave functions of the nearest oxygen ions remain approximately constant (Eremin et al. 1991). On the contrary, in a distant neighbourhood of the R ions the negative charges $O^{2-}(1)$ disappear in the CuO chains and $Cu^{2+}(1)$ ions transform into $Cu^{+}(1)$ (the crystal structure of the RBa₂Cu₃O_{6+x} compounds is described in sect. 6), so that the B_{20} parameter, containing the relatively large contribution from the electrostatic fields of the ionic charges, changes strongly.

At the end of this subsection it should be noted, that having a set of parameters B_{pq} attached to the crystallographic coordinate system one gets the opportunity (1) to describe the magnetic properties of a crystal at any appropriate value and direction of applied magnetic fields; (2) to obtain reasonable estimates of different effects due to electron-phonon interaction with only those model parameters which have been introduced to describe energy spectra in the static equilibrium lattice.

2.4. Electron-phonon interaction

The deformation of a lattice in general is accompanied by a redistribution of electron density and corresponding changes of ion multipole moments ΔM_l . Variations of crystal field parameters at deformation and polarization of the lattice,

$$\Delta B_{pq} = B_{pq}(X + \Delta X, M_l + \Delta M_l) - B_{pq}(X, M_l), \tag{50}$$

are usually presented as a series in static (uX + w), see eq. 10) or dynamic (ξ) displacements of ions and multipole moments ΔM_l . The corresponding operators of electron-deformation and electron-phonon interactions are given above in eqs. (18)-(20) and eq. (13). In the case of a uniform deformation of a lattice, the parameters of the operator (19) are related to the crystal field parameters in the following way (the origin of the coordinate system is placed at the lattice point M = 0, $\lambda = 0$, occupied by a lanthanide ion):

$$B_{p,\alpha\beta}^{q} = \frac{1}{2} \sum_{M,\lambda} \left[X_{\alpha} \begin{pmatrix} \lambda \\ M \end{pmatrix} \frac{\partial}{\partial X_{\beta} \begin{pmatrix} \lambda \\ M \end{pmatrix}} + X_{\beta} \begin{pmatrix} \lambda \\ M \end{pmatrix} \frac{\partial}{\partial X_{\alpha} \begin{pmatrix} \lambda \\ M \end{pmatrix}} \right] B_{pq}, \tag{51}$$

$$B_{p,a}^{\prime q}(\lambda) = \sum_{M} \frac{\partial}{\partial X_{\alpha} \begin{pmatrix} \lambda \\ M \end{pmatrix}} B_{pq} \quad (\lambda \neq 0),$$
(52)

$$B_{p,\alpha}^{\prime q}(0) = -\sum_{\lambda \neq 0} B_{p,\alpha}^{\prime q}(\lambda).$$
(53)

In principle, eqs. (51)–(53) contain additional terms due to the polarization of the lattice induced by its deformation, which may be significant when estimating the quadrupolar components of the crystal field. Expressions analogous to eqs. (51)–(53) are also easily obtained for parameters of the operator (20), for example (Dohm and Fulde 1975):

$$B_{p,\alpha\beta\gamma\delta}^{q} = \sum_{M\lambda} \left[X_{\{\alpha} \begin{pmatrix} \lambda \\ M \end{pmatrix} X_{\gamma} \begin{pmatrix} \lambda \\ M \end{pmatrix} \frac{\partial^{2}}{\partial X_{\beta} \begin{pmatrix} \lambda \\ M \end{pmatrix} \partial X_{\delta\}} \begin{pmatrix} \lambda \\ M \end{pmatrix}} - \frac{1}{2} \left(\delta_{\{\alpha\delta} X_{\beta} \begin{pmatrix} \lambda \\ M \end{pmatrix} \frac{\partial}{\partial X_{\gamma\}} \begin{pmatrix} \lambda \\ M \end{pmatrix}} + \delta_{\{\beta\gamma} X_{\delta} \begin{pmatrix} \lambda \\ M \end{pmatrix} \frac{\partial}{\partial X_{\alpha\}} \begin{pmatrix} \lambda \\ M \end{pmatrix}} \right) \right] B_{pq}$$

(braces indicate symmetrization with respect to permutations $\alpha \leftrightarrow \beta$, $\gamma \leftrightarrow \delta$, $\alpha\beta \leftrightarrow \gamma\delta$).

Since the spatial configuration of a lattice with excitation of long-wave acoustical vibrations can be described by the dynamical displacement tensor $u_{\alpha\beta}(q_{j_a})$ and dynamical displacements of sublattices $w(\lambda, q_{j_a})$ (with j_a the index of the acoustical branch of the vibrational spectrum), which are represented as

$$u_{\alpha\beta}(\boldsymbol{q}\boldsymbol{j}_{a}) = \frac{\mathrm{i}}{\sqrt{Nm}} e_{\alpha}(\boldsymbol{j}_{a}\boldsymbol{q}_{0}) q_{\beta} \mathcal{Q}(\boldsymbol{q}\boldsymbol{j}_{a}), \tag{54}$$

$$w_{\alpha}(\lambda, \boldsymbol{q} \boldsymbol{j}_{\mathrm{a}}) = \frac{\mathrm{i}}{\sqrt{Nm_{\lambda}}} \lim_{q \to 0} \left[\frac{1}{q_{\beta}} \mathrm{Im} \, e_{\alpha}(\lambda | \boldsymbol{q} \boldsymbol{j}_{\mathrm{a}}) \right] q_{\beta} \mathcal{Q}(\boldsymbol{q} \boldsymbol{j}_{\mathrm{a}}), \tag{55}$$

where *m* is the mass of a crystal cell. Coefficients of coupling with acoustical longwave vibrations in operator (13) may be presented by means of linear combinations of electron-deformation interaction parameters in eq. (19). The unit vector of the acoustic wave polarization $e(j_a q_0)$ in eq. (54) is defined as

$$\frac{e_{\alpha}(j_{a}\boldsymbol{q}_{0})}{\sqrt{m}} = \lim_{q \to 0} \frac{e_{\alpha}(\lambda | \boldsymbol{q} j_{a})}{\sqrt{m_{\lambda}}}, \qquad \boldsymbol{q}_{0} = \frac{\boldsymbol{q}}{|\boldsymbol{q}|},$$
(56)

The parameters of electron-deformation interaction for lanthanide ions in a lattice with a known structure can be easily estimated by means of the exchange charge model described above. In accordance with eq. (38) we separate out the contributions of multipolar fields and the exchange charge field:

$$B_{p,\alpha\beta}^{q} = \sum_{l} B_{p,\alpha\beta}^{q}{}^{(l)} + B_{p,\alpha\beta}^{q}(s),$$
(57)

$$B_{p,\alpha}^{\prime q}(\lambda) = \sum_{l} B_{p,\alpha}^{\prime q}(\lambda)^{(l)} + B_{p,\alpha}^{\prime q}(\lambda|s).$$
(58)

Substituting eq. (39) into eqs. (51), (52) and accounting for eq. (42), we obtain

$$B_{p,\alpha\beta}^{q}{}^{(0)} = \frac{1}{2}(p+1)K_{pq}(1-\sigma_{p})e^{2}\langle r^{p}\rangle\left(\frac{a_{p+1,0}}{a_{p,0}}\right)$$

$$\times \sum_{M\lambda}q_{\lambda}X\left(\frac{\lambda}{M}\right)^{-p-2}\left[X_{\alpha}\left(\frac{\lambda}{M}\right)W_{p,\beta}^{q}(\theta_{M\lambda},\phi_{M\lambda})\right]$$

$$+X_{\beta}\left(\frac{\lambda}{M}\right)W_{p,\alpha}^{q}(\theta_{M\lambda},\phi_{M\lambda})\right],$$

$$B_{p,\alpha}^{\prime q}(\lambda)^{(0)} = e^{2}q_{\lambda}(p+1)K_{pq}(1-\sigma_{p})\langle r^{p}\rangle\left(\frac{a_{p+1,0}}{a_{p,0}}\right)$$

$$\times \sum_{M\lambda}X\left(\frac{\lambda}{M}\right)^{-p-2}\left[W_{p,\alpha}^{q}(\theta_{M\lambda},\phi_{M\lambda})\right].$$
(60)

Using eqs. (42) and (43), it is possible to obtain an explicit form of contributions of ionic multipolar moments into expressions (57), (58) (Malkin 1987). The contributions of exchange charges to electron-phonon interaction parameters are

$$B_{p,\alpha\beta}^{q}(s) = -\frac{2p+1}{7} K_{pq} e^{2} \\ \times \sum_{\nu} R_{\nu}^{-2} \left\{ (p+1) \frac{a_{p+1,0}}{a_{p,0}} S_{p}(R_{\nu}) \left[X_{\alpha}(\nu) W_{p,\beta}^{q}(\theta_{\nu},\phi_{\nu}) + X_{\beta}(\nu) W_{p,\alpha}^{q}(\theta_{\nu},\phi_{\nu}) \right] \right. \\ \left. -2X_{\alpha}(\nu) X_{\beta}(\nu) O_{p}^{q}(\theta_{\nu},\phi_{\nu}) \left[p \frac{S_{p}(R_{\nu})}{R_{\nu}} + \frac{d}{dR_{\nu}} S_{p}(R_{\nu}) \right] \right\},$$
(61)

$$B_{p,a}^{\prime q}(\lambda|s) = -\frac{2(2p+1)}{7} K_{pq} e^{2} \\ \times \sum_{\nu \in \lambda} R_{\nu}^{-2} \Biggl\{ (p+1) \frac{a_{p+1,0}}{a_{p,0}} W_{p,a}^{q}(\theta_{\nu}, \phi_{\nu}) S_{p}(R_{\nu}) \\ -X_{\alpha}(\nu) O_{p}^{q}(\theta_{\nu}, \phi_{\nu}) \left[p \frac{S_{p}(R_{\nu})}{R_{\nu}} + \frac{d}{dR_{\nu}} S_{p}(R_{\nu}) \right] \Biggr\}.$$
(62)

The summation in eq. (62) is extended over ligands from the sublattice λ . An explicit form of all parameters of the operator $\mathcal{H}_{e-1}^{(2)}$ nonlinear in lattice variables (eq. 20) may be found in a similar way. If p=2, conditionally converging lattice sums in eq. (59) should be calculated by use of the Ewald method:

$$B_{2,\alpha\beta}^{q}{}^{(0)} = -(1-\sigma_2) \left\langle r^2 \right\rangle e^2 \sum_{\lambda} q(\lambda) Q_{q,\alpha\beta}(0\lambda); \tag{63}$$

where

 $Q_{0,\alpha\beta} = \frac{1}{4}Q_{zz,\alpha\beta},$ $Q_{1,\alpha\beta} = Q_{xz,\alpha\beta},$ $Q_{-1,\alpha\beta} = Q_{yz,\alpha\beta},$ $Q_{2,\alpha\beta} = \frac{1}{4}(Q_{xx,\alpha\beta} - Q_{yy,\alpha\beta}),$ $Q_{-2,\alpha\beta} = \frac{1}{2}Q_{xy,\alpha\beta};$

 $Q_{\alpha\beta,\gamma\delta}$ are rapidly converging sums over direct and reciprocal lattices (see eqs. 45–47):

$$Q_{\alpha\beta,\gamma\delta}(\lambda\lambda') = \frac{C^3}{\sqrt{\pi}} \sum_{M} x^{-2} \left\{ \left(2\delta_{\alpha\beta}x_{\gamma}x_{\delta} + \delta_{\beta\delta}x_{\alpha}x_{\gamma} + \delta_{\beta\gamma}x_{\alpha}x_{\delta} + \delta_{\alpha\gamma}x_{\beta}x_{\delta} + \delta_{\alpha\delta}x_{\beta}x_{\gamma} \right) \\ \times \left[2e^{-x^2} + \frac{3}{x^2}\Phi(x) \right] \\ + 2 \left[4e^{-x^2} + \frac{10}{x^2}e^{-x^2} + \frac{15}{x^4}\Phi(x) \right] x_{\alpha}x_{\beta}x_{\gamma}x_{\delta} \right\} \\ + \frac{2\pi}{v} \sum_{h\neq 0} \left\{ 2\delta_{\gamma\delta}y_{\alpha}y_{\beta} + \delta_{\alpha\gamma}y_{\beta}y_{\delta} + \delta_{\alpha\delta}y_{\gamma}y_{\beta} + \delta_{\beta\delta}y_{\alpha}y_{\gamma} + \delta_{\beta\gamma}y_{\alpha}y_{\delta} \\ - 4y_{\alpha}y_{\beta}y_{\gamma}y_{\delta} \left(\frac{1}{y^2} + \frac{\pi^2}{C^2} \right) G(h) \cos \left[2\pi y(h) \cdot X \begin{pmatrix} \lambda & \lambda' \\ 0 & 0 \end{pmatrix} \right] \right\}.$$
(64)

In the sum over M the term with M=0 should be excluded at $\lambda = \lambda'$.

The quantities $B_{p,\alpha\beta}^q$, $B_{p,\alpha}^{\prime q}(\lambda)$ form a complete set of independent parameters of the Hamiltonian of orbit-lattice interaction, linear in lattice variables. The response of a paramagnetic crystal to different external perturbations (electric or magnetic field, hydrostatic pressure, uniaxial pressure), the dependence of spectra on temperature, and the spin-phonon interaction, are all determined by different combinations of these parameters.

2.5. Free energy of a crystal and magnetoelastic interactions

In this subsection we shall consider methods of calculation of magnetoelastic characteristics of the lanthanide compounds, putting off the discussion of specific systems to the following paragraphs. The lattice structure and magnetization of the crystals are determined by the free energy minimum condition. A rigorous analytical calculation of free energy for two interacting subsystems of a crystal (4f electrons and phonons) is impossible, however, the basic peculiarities of temperature-dependent responses to applied stationary perturbations can be qualitatively described by an effective Hamiltonian of the electronic subsystem, deduced within the framework of a self-consistent field approximation. Despite crude approximations the theoretical estimates of thermodynamic parameters differ from experimental data by no more than an order of magnitude.

An effective Hamiltonian of the electron subsystem can be constructed with the displaced phonon operator method (Elliott et al. 1972, Young 1975) or the method of canonical transformation (Mutscheller and Wagner 1986); analoguous results are given by a perturbation method in the second order in the electron-phonon interaction \mathcal{H}_{e-ph} (13) (Baker 1971).

The transformation

$$Q'(-qj) = Q(-qj) + \omega_j^{-2}(q) \sum_{pq\lambda} B_p^q(\lambda|qj) O_p^q(\lambda|q),$$
(65)

with

$$O_p^q(\lambda|\boldsymbol{q}) = \frac{1}{\sqrt{N}} \sum_{M} \exp\left[i\boldsymbol{q} \cdot \boldsymbol{X}\begin{pmatrix}\lambda\\M\end{pmatrix}\right] O_p^q(\lambda M), \tag{66}$$

introduces the following two-particle interaction operator:

$$\Delta \mathcal{H}_2 = -\sum_{\lambda\lambda'} \sum_{\boldsymbol{q}} \sum_{pp'qq'} J_{pp'}^{qq'} (\lambda\lambda'|\boldsymbol{q}) O_p^q(\lambda|\boldsymbol{q}) O_{p'}^{q'}(\lambda'|-\boldsymbol{q}),$$
(67)

into the crystal Hamiltonian instead of electron-phonon interaction (13) linear in lattice normal coordinates. In eq. (67) we have

$$J_{pp'}^{qq'}(\lambda\lambda'|\boldsymbol{q}) = \sum_{j} K_{pp'}^{qq'}(\lambda\lambda'|\boldsymbol{q}j) - \left(\frac{1}{N}\right) \delta_{\lambda\lambda'} \sum_{\boldsymbol{q}j} K_{pp'}^{qq'}(\lambda\lambda'|\boldsymbol{q}'j), \tag{68}$$

$$K_{pp'}^{qq'}(\lambda\lambda'|\boldsymbol{q}) = \omega_j^{-2}(\boldsymbol{q}) B_p^q(\lambda|\boldsymbol{q}j) B_{p'}^{q'}(\lambda'|-\boldsymbol{q}j).$$
⁽⁶⁹⁾

Disregarding changes in the R ion spectral parameters, induced by electron-phonon interaction [vibronic reduction takes place if operator (13) does not commute with \mathcal{H}_0 and \mathcal{H}_Z , Ham (1965)], the Hamiltonian of the electronic subsystem in a self-consistent field approximation may be written as

$$\mathcal{H} = \frac{1}{2}N\sum_{\lambda\lambda'} \left\{ \left\langle J_{a}(\lambda) \right\rangle p_{a\beta}(\lambda\lambda') \left\langle J_{\beta}(\lambda') \right\rangle + \sum_{pp'qq'} \left\langle O_{p}^{q}(\lambda) \right\rangle J_{pp'}^{qq'}(\lambda\lambda'|0) \left\langle O_{p'}^{q'}(\lambda') \right\rangle \right\} + \sum_{\lambda\mathcal{M}} \mathcal{H}_{\mathsf{R}, \text{eff}}(\lambda\mathcal{M}).$$
(70)

In the derivation of eq. (70) it has been assumed that the mean values of the electron operators $\langle J(\lambda M) \rangle = \langle J(\lambda) \rangle$, $\langle O_p^q(\lambda M) \rangle = \langle O_p^q(\lambda) \rangle = (1/\sqrt{N}) \langle O_p^q(\lambda, q = 0) \rangle$ are similar for all lanthanide ions of the sublattice λ . At the same time a possible phase transition does not affect the elementary cell; the consideration of electronic orbital ordering in other points of the Brillouin zone may be fulfilled in the same way.

The first term in eq. (70) corresponds to magnetic dipole-dipole and exchange interactions (the terms $A_{\alpha\beta}\begin{pmatrix}\lambda & \lambda'\\M & M'\end{pmatrix}J_{\alpha}(\lambda M)J_{\beta}(\lambda'M')$ in eq. 32). The magnetic

330

molecular field parameters $p_{\alpha\beta}(\lambda\lambda')$, determining the local magnetic field $H_{loc}(\lambda)$ at lattice points (λM) ,

$$H_{\text{loc, }\alpha}(\lambda) = H_{0\alpha} - (g_{J}\mu_{B})^{-1} \sum_{\lambda'} p_{\alpha\beta}(\lambda\lambda') \left\langle J_{\beta}(\lambda') \right\rangle,$$
(71)

are equal to

$$p_{\alpha\beta}(\lambda\lambda') = (g_{\rm J}\mu_{\rm B})^2 \left\{ Q_{\alpha\beta}(\lambda\lambda') - \left(\frac{1}{\nu}\right) D_{\alpha\beta} \right\} - \sum_M A_{\alpha\beta} \begin{pmatrix} \lambda & \lambda' \\ 0 & M \end{pmatrix}, \tag{72}$$

where $D_{\alpha\beta}$ are demagnetization factors, satisfying the condition $\sum_{\alpha} D_{\alpha\alpha} = 4\pi$, and the Lorentz field factors $Q_{\alpha\beta}(\lambda\lambda')$ are defined by eq. (45). In eq. (68) for the parameters $J_{pp'}^{qq'}(\lambda\lambda'|0)$ of a self-consistent field, responsible for the interaction between the lanthanide ions via the phonon field, the summation in the first term extends only to the optical branches of a lattice vibrational spectrum; contributions of acoustical branches at $q \to 0$ are specified by the operator (19).

The effective single-ion Hamiltonian $\mathcal{H}_{R, eff}$ is obtained from eq. (4) by substituting local field for applied field and substituting the operator

$$\Delta \mathcal{H}_{\mathsf{R}}(\lambda M) = -\sum_{\lambda'} \sum_{pp'qq'} \left\langle O_p^q(\lambda') \right\rangle J_{pp'}^{qq'}(\lambda \lambda'|0) O_p^q(\lambda M)$$
(73)

for \mathcal{H}_{e-ph} . Using the operator (70) one may simply calculate the free energy of a crystal for different types of electronic ordering. Let an elementary cell contain *n* magnetically equivalent lanthanide ions and suppose that $\langle J_{\alpha}(\lambda) \rangle = \langle J_{\alpha} \rangle$, $\langle O_{p}^{q}(\lambda) \rangle = \langle O_{p}^{q} \rangle$ (para- or ferromagnetic state). For the sake of brevity we shall further use matrix notation in the elementary cell basis and in the electronic operator space; for instance

$$\sum_{\lambda} A_{\alpha}(\lambda) B_{\alpha}(\lambda) = \boldsymbol{A} \cdot \boldsymbol{B}, \qquad \sum_{pq} A_{p}^{q} B_{p}^{q} = \boldsymbol{A} : \boldsymbol{B}.$$

Introducing the electronic magnetization

$$\boldsymbol{M} = -\left(\frac{n}{\nu}\right) \boldsymbol{g}_{\mathrm{J}} \boldsymbol{\mu}_{\mathrm{B}} \left\langle \boldsymbol{J} \right\rangle, \tag{74}$$

we obtain the specific (per cell) free energy of a crystal in the following form

$$F = vE_{\text{lat}} + \frac{1}{2}n \langle \boldsymbol{O} \rangle : \boldsymbol{\eta} : \langle \boldsymbol{O} \rangle + \frac{1}{2}vM\boldsymbol{\Lambda}\boldsymbol{M} + nf(\langle \boldsymbol{O} \rangle, \boldsymbol{M}, \boldsymbol{e}, \boldsymbol{w}),$$
(75)

where E_{lat} is the energy (27) of the elastic-deformed lattice at $E_0 = 0$ (electric field effects will be considered separately below),

$$\Lambda_{\alpha\beta} = \left(\frac{\nu}{n}\right) \left(g_{\rm J}\mu_{\rm B}\right)^{-2} \sum_{\lambda'} p_{\alpha\beta}(\lambda\lambda'),\tag{76}$$

$$\eta_{pp'}^{qq'} = \sum_{\lambda'} J_{pp'}^{qq'}(\lambda\lambda'|0);$$
(77)

and f is the single-ion free energy equal to

$$f(\langle \boldsymbol{O} \rangle, \boldsymbol{M}, \boldsymbol{e}, \boldsymbol{w}) = -k_{\rm B}T \ln \operatorname{Sp} \exp\left(\frac{-\mathcal{H}_{\rm R, eff}}{k_{\rm B}T}\right).$$
 (78)

Nuclear magnetism problems will be considered in the following sections, here we represent a single-ion effective Hamiltonian in the form

$$\mathcal{H}_{\mathrm{R, eff}} = \mathcal{H}_{0} + (g_{\mathrm{J}}\mu_{\mathrm{B}})(\boldsymbol{H}_{0} + \boldsymbol{M}\boldsymbol{\Lambda})\boldsymbol{J} + \mathcal{H}_{\mathrm{e}-\mathrm{I}} - \langle \boldsymbol{O} \rangle : \boldsymbol{\eta} : \langle \boldsymbol{O} \rangle.$$
(79)

The main magnetoelastic effects, such as magnetostriction and alterations of sound velocity in a magnetic field, may be described by considering only those terms in the corresponding series expansion of the free energy, which are linear and quadratic in the deformation parameters $u_{\alpha\beta}$, $w_{\alpha}(\lambda)$. It should be noted that the function f depends on the deformation parameters both explicitly, through \mathcal{H}_{e-1} , and implicitly, because of the dependence of molecular field constants on the lattice structure:

$$\Lambda_{\alpha\beta} = \Lambda_{0\alpha\beta} + \Lambda^{(e)}_{\alpha\beta,\gamma\delta} e_{\gamma\delta} + \sum_{\lambda} \Lambda^{(w)}_{\alpha\beta,\gamma}(\lambda) w_{\gamma}(\lambda) + \cdots$$
(80)

Actually the quantities $\Lambda^{(e)}$, $\Lambda^{(w)}$ are determined by the two-particle mechanism of magnetoelastic coupling. Neglecting anharmonic terms of the lattice potential energy (a change of the vibrational spectra at deformation), it is possible to disregard the dependence of the self-consistent field parameters η on the deformation parameters.

The minimum conditions for the free energy:

$$\frac{\partial F}{\partial \left\langle O_p^k \right\rangle} = 0, \tag{81}$$

$$\frac{\partial F}{\partial M_{\alpha}} = 0, \tag{82}$$

$$\frac{\partial F}{\partial e_{\alpha\beta}} = 0,\tag{83}$$

$$\frac{\partial F}{\partial w_a(\lambda)} = 0,\tag{84}$$

give a system of coupled equations determining equilibrium values of order parameters of the electronic subsystem, magnetization and the parameters of macro- $(e_{\alpha\beta})$ and microscopic $(w_{\alpha}(\lambda))$ deformation as functions of an applied magnetic field, applied stress and temperature. Generally these equations can not be solved in an analytical form, so the results of the calculations given below refer to specific situations with definite restrictions on the structure of a ground multiplet spectrum or on the magnitude of an applied magnetic field.

An implicit dependence of the system characteristics on a magnetic field may be obtained, assuming the eigenvalues and eigenfunctions of the operator $\mathcal{H}_0 + \mathcal{H}_Z$ are known,

$$(\mathcal{H}_0 + \mathcal{H}_Z) |i\rangle = \varepsilon_i |i\rangle. \tag{85}$$

Let us introduce the generalized single-ion susceptibility

$$\chi(\widehat{A},\widehat{B}) = \frac{1}{k_{\mathrm{B}}T} \left[\sum_{i} \sum_{i'} w_{i} \left\langle i \left| \widehat{A} \right| i' \right\rangle \left\langle i' \left| \widehat{B} \right| i \right\rangle - \left\langle A \right\rangle_{0} \left\langle B \right\rangle_{0} \right] + \sum_{i} w_{i} \sum_{j \neq i} (\varepsilon_{j} - \varepsilon_{i})^{-1} \left(\left\langle i \left| \widehat{A} \right| j \right\rangle \left\langle j \left| \widehat{B} \right| i \right\rangle + \left\langle i \left| \widehat{B} \right| j \right\rangle \left\langle j \left| \widehat{A} \right| i \right\rangle \right),$$
(86)

where \hat{A} , \hat{B} are the Hermitian operators, w_i is the population of the *i*-th state,

$$w_i = \exp\left(-\frac{\varepsilon_i}{k_{\rm B}T}\right) \left[\sum_i \exp\left(-\frac{\varepsilon_i}{k_{\rm B}T}\right)\right]^{-1},\tag{87}$$

and $\langle \cdots \rangle_0$ denotes the statistical average

$$\langle A \rangle_0 = \sum_i w_i \left\langle i \left| \widehat{A} \right| i \right\rangle.$$
(88)

The index *i'* denotes the states with energy $\varepsilon_{i'} = \varepsilon_i$, so for nondegenerate states *i* there is no sum over *i'*. Considering the operator $\mathcal{H}_{e-1} - \langle \boldsymbol{O} \rangle$: $\boldsymbol{\eta}$: \boldsymbol{O} in eq. (79) to be the perturbation, one obtains the single-ion free energy (78) in the following form:

$$f = f_0 + \langle V \rangle_0 + \left\langle \mathcal{H}_{e-1}^{(2)}(\boldsymbol{\theta} = 0) + \frac{1}{2}g_J \mu_B[(\boldsymbol{H}\boldsymbol{\theta})(\boldsymbol{J}\boldsymbol{\theta}) - (\boldsymbol{H}\boldsymbol{J})\boldsymbol{\theta}^2] \right\rangle_0 - \frac{1}{2}\chi(V,V), \quad (89)$$

where f_0 is the free energy of an ion in a crystal and local magnetic fields,

$$V = (\boldsymbol{B} \cdot \boldsymbol{e} + \boldsymbol{B}' \cdot \boldsymbol{w} - \langle \boldsymbol{O} \rangle : \boldsymbol{\eta}) : \boldsymbol{O} + g_{\mathrm{J}} \mu_{\mathrm{B}} \boldsymbol{J} (\boldsymbol{H} \times \boldsymbol{\theta}), \tag{90}$$

and upon inserting the operator $\mathcal{H}_{e-1}^{(2)}(20)$ into eq. (89) $\boldsymbol{\theta}$ should equal zero. Thus, the explicit dependence of the free energy on the rotation angle $\boldsymbol{\theta}$ shows, that the electron-rotation interaction affects the lanthanide ion spectrum only in the presence of an applied field \boldsymbol{H}_0 (Bonsall and Melcher 1976). The influence of electron-rotation interaction on static and quasistatic magnetoelastic characteristics can be analyzed by directly applying

the rotation (15) to a magnetic field H_0 in the Zeeman operator. The terms in eq. (89) which are linear in the rotational angle θ and determine the rotating moment operating on a crystal, may be omitted when considering clamped samples.

Inserting eq. (89) into eq. (75) and using eq. (81), we obtain a linear relation between components of the electronic order parameter and the lattice deformation parameters:

$$\langle \boldsymbol{O} \rangle = (1 - \boldsymbol{\chi}_0 : \boldsymbol{\eta})^{-1} : \left[\langle \boldsymbol{O} \rangle_0 : \boldsymbol{\chi}_0 : (\boldsymbol{B} \cdot \boldsymbol{e} + \boldsymbol{B}' \cdot \boldsymbol{w}) - g_J \mu_B (\boldsymbol{H}_0 \times \boldsymbol{\theta})_a \boldsymbol{\chi}_{0a} \right],$$
(91)

where χ_0 , $\chi_{0\alpha}$, are matrices with components $\chi(O_p^k, O_{p'}^{k'})$ and $\chi_0(O_p^k, J_\alpha)$, respectively. In the vicinity of the electronic orbital ordering point the restriction in terms of the second order in the expansion (89) becomes incorrect. Taking into account eq. (91), the free energy of a crystal takes the form

$$F = vE_{\text{lat}}(T) + nf_0 + \frac{1}{2}vMAM - \frac{1}{2}n\langle O \rangle_0 : \boldsymbol{\eta} : (1 - \boldsymbol{\chi}_0 : \boldsymbol{\eta})^{-1} : \langle O \rangle_0 + n(\boldsymbol{B} \cdot \boldsymbol{e} + \boldsymbol{B}' \cdot \boldsymbol{w}) : (1 - \boldsymbol{\chi}_0 : \boldsymbol{\eta})^{-1} : \langle O \rangle_0 + \Delta F.$$
(92)

In eq. (92) $E_{\text{lat}}(T)$ is the energy of the elastic-deformed crystal involving the corresponding contributions of the electronic subsystem, which retains the structure of eq. (20), though with renormalized matrices of coefficients:

$$\boldsymbol{a}(T) = \boldsymbol{a} - \frac{n}{v} \boldsymbol{B}' : (1 - \boldsymbol{\chi}_0 : \boldsymbol{\eta})^{-1} : \boldsymbol{\chi}_0 : \boldsymbol{B}' + \frac{n}{v} \langle \boldsymbol{O} \rangle_0 : \boldsymbol{D}',$$
(93)

$$\boldsymbol{b}(T) = \boldsymbol{b} - \frac{n}{v} \boldsymbol{B}' : (1 - \boldsymbol{\chi}_0 : \boldsymbol{\eta})^{-1} : \boldsymbol{\chi}_0 : \boldsymbol{B} + \frac{n}{v} \langle \boldsymbol{O} \rangle_0 : \boldsymbol{D}'',$$
(94)

$$\widehat{\boldsymbol{C}}(T) = \widehat{\boldsymbol{C}} - \frac{n}{v}\boldsymbol{B} : (1 - \boldsymbol{\chi}_0 : \boldsymbol{\eta})^{-1} : \boldsymbol{\chi}_0 : \boldsymbol{B} + \frac{n}{v} \langle \boldsymbol{O} \rangle_0 : \boldsymbol{D}.$$
(95)

The second and third terms in eqs. (93)-(95) represent contributions of linear and quadratic electron-deformation interactions, respectively. The last term in eq. (92),

$$\Delta F = \frac{n}{2} \sum_{pq} B_{p,\alpha\beta}^{q} u_{\gamma\alpha} u_{\gamma\beta} \left\langle O_{p}^{q} \right\rangle_{0}$$

$$- ng_{J} \mu_{B} (\boldsymbol{H}_{0} \times \boldsymbol{\theta})_{\alpha} \boldsymbol{\chi}_{0\alpha} : (1 - \boldsymbol{\chi}_{0} : \boldsymbol{\eta})^{-1} : (\boldsymbol{B}\boldsymbol{e} + \boldsymbol{B}'\boldsymbol{w})$$

$$- \frac{1}{2} ng_{J} \mu_{B} (\boldsymbol{H}_{0} \times \boldsymbol{\theta})_{\alpha} \left[\boldsymbol{\chi}_{\alpha\beta} + \boldsymbol{\chi}_{0\alpha} : \boldsymbol{\eta} : (1 - \boldsymbol{\chi}_{0} : \boldsymbol{\eta})^{-1} : \boldsymbol{\chi}_{0\beta} \right] (\boldsymbol{H}_{0} \times \boldsymbol{\theta})_{\beta},$$
(96)

corresponds to the contributions of linear electron-rotation interaction and nonlinear term of the finite deformation tensor (14). Here $\chi_{\alpha\beta} = \chi(J_{\alpha}, J_{\beta})$ (see eq. 86).

The coefficients at e and w in the crystal free energy correspond to effective external and internal strains. The condition (84) results in a linear relation between characteristics of macro- and microscopic deformations:

$$\boldsymbol{w} = -\boldsymbol{a}(T)^{-1} \cdot \boldsymbol{b}(T)\boldsymbol{e} + \Delta \boldsymbol{w}, \tag{97}$$

$$\Delta \boldsymbol{w} = -\frac{n}{v} \boldsymbol{a}(T)^{-1} \cdot \boldsymbol{B}'(T) : \langle \boldsymbol{O} \rangle_0, \qquad (98)$$

and eq. (83) determines the equilibrium structure of a lattice, depending on the temperature, the applied magnetic field and the applied stress σ :

$$\boldsymbol{e} = -\frac{n}{v} \boldsymbol{S}(T) \, \boldsymbol{B}^{(r)}(T) : \langle \boldsymbol{O} \rangle_0 + \boldsymbol{S}(T) \, \boldsymbol{\sigma}.$$
⁽⁹⁹⁾

Displacements Δw of sublattices differ from zero only in the presence of internal stress, in particular, in magnetic and electric fields. The parameter matrices B'(T) and $B^{(r)}(T)$ represent renormalized coefficients of the linear magnetoelastic coupling:

$$B'(T) = (1 - \eta : \chi_0)^{-1} : B',$$
(100)

$$\boldsymbol{B}^{(r)}(T) = (1 - \boldsymbol{\eta} : \boldsymbol{\chi}_0)^{-1} : \boldsymbol{B}^{(r)},$$
(101)

$$\boldsymbol{B}^{(r)} = \boldsymbol{B} - \boldsymbol{b}(T) \cdot \boldsymbol{a}(T)^{-1} \cdot \boldsymbol{B}'.$$
(102)

The tensor of elastic compliancy $S(T) = C(T)^{-1}$, and the elastic constant matrix (ignoring the terms due to electron-rotation interaction) is equal to:

$$\boldsymbol{C}(T) = \widehat{\boldsymbol{C}}(T) - \boldsymbol{b}(T) \cdot \boldsymbol{a}(T)^{-1} \cdot \boldsymbol{b}(T).$$
(103)

The free energy of a crystal in a magnetically ordered phase or in an applied magnetic field may be presented only as an expansion in powers of displacement tensor components $u_{\alpha\beta}$ (see eqs. 92 and 96); the contributions of finite deformations and electron-rotation interactions to isothermal elastic constants,

$$C_{\alpha\beta\gamma\delta} = \frac{\partial^2 F}{\partial u_{\alpha\beta}\partial u_{\gamma\delta}} \tag{104}$$

break the symmetry relative to the permutation of indices α, β and γ, δ (Melcher 1976).

A two-particle mechanism of magnetoelastic coupling gives additional contributions into the above-mentioned expressions for deformation parameters and elastic constants. Confining the constants in expansion (80) of the self-consistent magnetic field to the terms linear in deformation parameters and using an equilibrium condition (82), we obtain, in particular, additional terms to eqs. (93)–(95) in the form of

$$\Delta \widehat{\boldsymbol{C}}(T) = \boldsymbol{M}_0 \boldsymbol{\Lambda}^{(e)} \boldsymbol{\chi}' \boldsymbol{\Lambda}^{(e)} \boldsymbol{M}_0 - 2\boldsymbol{M}_0 (1 - \boldsymbol{\chi}' \boldsymbol{\Lambda}_0) \boldsymbol{M}^{(e)} \boldsymbol{\Lambda}^{(e)} - (1 - \boldsymbol{\chi}' \boldsymbol{\Lambda}_0) \boldsymbol{M}^{(e)} \boldsymbol{\Lambda} \boldsymbol{M}^{(e)},$$
(105)

where M_0 is the equilibrium magnetization at e=0, w=0:

$$\boldsymbol{M}_{0} = -\frac{n}{v} \nabla_{\boldsymbol{H}} f_{0}(\boldsymbol{H}_{0} + \boldsymbol{\Lambda}_{0} \boldsymbol{M}_{0}), \qquad (106)$$

 χ' is the single-ion magnetic susceptibility:

$$\boldsymbol{\chi}' = -\frac{n}{v} \nabla_{\boldsymbol{H}} \nabla_{\boldsymbol{H}} f_0 = +\frac{n}{v} (g_{\mathrm{J}} \mu_{\mathrm{B}})^2 \boldsymbol{\chi}(\boldsymbol{J}, \boldsymbol{J})$$
(107)

and $M^{(e)}$ is the first derivative of magnetization M with respect to deformation e (tensor of piezomagnetic constants):

$$\boldsymbol{M}^{(e)} = (1 - \boldsymbol{\chi}' \boldsymbol{\Lambda}_0)^{-1} \left[\boldsymbol{\chi}' \boldsymbol{\Lambda}^{(e)} \boldsymbol{M}_0 - \frac{n}{v} \boldsymbol{B} : \nabla_{\boldsymbol{H}} \langle \boldsymbol{O} \rangle_0 \right].$$
(108)

The lattice deformation due to two-particle magnetoelastic interactions is determined by the equations

$$\boldsymbol{e} = \frac{1}{2}\boldsymbol{S}(T)\boldsymbol{\Lambda}^{(r)}\boldsymbol{M}_{0}\boldsymbol{M}_{0}; \qquad \Delta \boldsymbol{w} = \frac{1}{2}\boldsymbol{a}(T)^{-1} \cdot \boldsymbol{\Lambda}^{(w)}\boldsymbol{M}_{0}\boldsymbol{M}_{0}, \tag{109}$$

where

$$\boldsymbol{\Lambda}^{(r)} = \boldsymbol{\Lambda}^{(e)} - \boldsymbol{b}(T) \cdot \boldsymbol{a}(T)^{-1} \cdot \boldsymbol{\Lambda}^{(w)}$$
(110)

are renormalized coefficients of the expansion (80). As we shall see in sect. 4, the two-particle mechanism of magnetoelastic coupling may prevail in some conditions (particularly in systems with mainly the dipole-dipole mechanism of the magnetic ordering).

In the absence of external fields ($\sigma = 0$, $H_0 = 0$) eqs. (99) and (108) describe the contribution of the electron subsystem to the thermal expansion of a lattice (Abdulsabirov et al. 1993) and also a spontaneous striction accompanying the electronic or magnetic ordering. In the immediate vicinity of the transition point, owing to the divergence of effective susceptibilities, it might be necessary to take into account the higher-order terms in the expansion of the crystal free energy. Analytical results in this case may be obtained with the pseudospin formalism. Corresponding examples will be considered in the following sections of this chapter.

The relative change of the sample length in the direction of a unit vector n is equal to

$$\frac{\Delta L}{L} = n_{\alpha} n_{\beta} e_{\alpha\beta}. \tag{111}$$

When experimental values of elastic constants are used, the striction depends linearly on effective coupling constants given by eq. (101), and induced magnetostriction anisotropy

measured at $H_0 \neq 0$ makes it possible to obtain some information on the magnitudes of electron-deformation interaction constants. It should be noted that, in general, the deformation of the lattice in a magnetic field is not equivalent to the deformation conditioned by an external stress (for instance, by uniaxial pressure), because there are no internal stresses in mechanically pressed samples.

The structure of the Hamiltonian of the orbit-lattice interaction and calculations of effective coupling constants are considerably simplified when the symmetry properties of a lattice are utilized. It is possible to introduce linear combinations of the deformation tensor components $e_{\lambda}(\Gamma_i^j)$ and of sublattice displacements $w_{\lambda}(\Gamma_i^j)$, which are transformed according to irreducible representations of a symmetry group at the Γ -point of the Brillouin zone (q=0). Here indices *i*, *j* and λ denote the type, number and row of representation, respectively. In particular, the operator (19) takes the form

$$\mathcal{H}_{\mathsf{e}-\mathsf{l}}^{(1)} = \sum_{pq} \sum_{ij\lambda} \left[B_{p\lambda}^{q}(\Gamma_{i}^{j}) e_{\lambda}(\Gamma_{i}^{j}) + B_{p\lambda}^{\prime q}(\Gamma_{i}^{j}) w_{\lambda}(\Gamma_{i}^{j}) \right] O_{p}^{q}(J) + \mathbf{i}[H_{0}, \boldsymbol{\theta}J].$$
(112)

When choosing normal lattice modes at the Γ -point as a basis in the space of the displacement vectors of sublattices, we obtain renormalized constants of coupling with macroscopic deformation (eq. 105) in the following form:

$$B_{p\lambda}^{(r)q}(\Gamma_i^j) = B_{p\lambda}^q(\Gamma_i^j) - \sum_l B_{p\lambda}^{\prime q}(\Gamma_i^l) \,\omega^{-2}(\Gamma_i^l) \,b_\lambda(\Gamma_i^l \Gamma_i^j),\tag{113}$$

where $b_{\lambda}(\Gamma_i^l \Gamma_i^j)$ are linear combinations of the components of matrix **b**, and the matrix **a** is substituted by the dynamic matrix $D(q=0) = m^{-1/2} a m^{-1/2}$ at the center of the Brillouin zone (**m** is the matrix of ionic masses, diagonal in the site representation: $m_{\alpha\beta}(ll') = m_{\lambda}\delta_{\alpha\beta}\delta_{\lambda\lambda'}$) with eigenvectors $e_{\alpha}(\lambda|0j)$ and eigenvalues $\omega_j^2(0) = \omega^2(\Gamma_j^j)$. The matrices D(q=0) and **a** are singular $(\omega_{ja}(0)=0)$; three rows and three columns with index λ_0 are omitted when the matrix a^{-1} is constructed, i.e. the sublattice λ_0 is fixed in space and only relative displacements of other sublattices are considered. The obtained matrix of the rank 3(r-1) is inverted (r is the number of atoms in an elementary cell) and then supplemented by three zero rows and columns, so that the order of matrix a^{-1} becomes $3r \times 3r$ (Born and Huang 1954).

In a lattice with an inversion center, the displacements $w(\lambda)$ and dipolar moments induced by deformation are equal in value and opposite in sign for sublattices transforming into each other at inversion. In this case the effective constants of lanthanide ion coupling with macroscopic deformation contain only contributions from lattice modes active in Raman scattering, which transform according to even irreducible representations of the Γ -point symmetry group. A complete number of independent parameters in the Hamiltonian of the electron-deformation interaction is so large (except for the case of a cubic symmetry), that it is practically impossible to determine them from measurements of the magnetic and magnetoelastic characteristics; usually it appears possible to estimate only some linear and bilinear combinations of parameters $B_{p\lambda}^{(r)q}(\Gamma_i^j)$, $B_{p\lambda}'(\Gamma_i^j)$.

L.K. AMINOV et al.

Some information on coupling parameters with sublattice displacements $B'_{p\lambda}(\Gamma_i^j)$ may be drawn from the temperature and magnetic field dependences of Raman scattering and infrared absorption spectra in rare-earth paramagnets (Kupchikov et al. 1987, Dorfler and Schaack 1985, Dahl and Schaack 1986). The most simple and informative method to study parameters of lanthanide ion coupling with macroscopic deformation is optical piezospectroscopy. Representing the deformation parameters e, w through the tensor of applied stress σ (see eqs. 97 and 99) and inserting them into eq. (91) and then into operator (19), one obtains the Hamiltonian of the lanthanide ion interaction with an applied stress in the form

$$\mathcal{H}_{\sigma} = \sum_{pq} B^{(r)q}_{\ \ \ \ \ \ \rho,\alpha\beta}(T) S_{\alpha\beta\gamma\delta} \sigma_{\gamma\delta} O_p^q.$$
(114)

By measuring the shifts and splittings induced by uniaxial pressure, applied in different directions ($\sigma_{\alpha\beta} = -pl_{\alpha}l_{\beta}$, p is the magnitude of pressure, l is the unit vector in the stretch direction), it is possible to obtain a complete set of parameters $B^{(r)}(T)$.

By now a sufficient amount of information, necessary for determining coupling constants with definite lattice deformations $e_{\lambda}(\Gamma_i^j)$, has been obtained as part of piezospectroscopic investigations of crystals with the zircon and scheelite structures. The elastic energy of the tetragonal lattices of RMO₄ and LiRF₄ crystals may be written as an expansion in symmetrized deformations conforming to irreducible representations of D_{4h} and C_{4h} factor-groups:

$$\mathcal{H}_{\text{lat}} = \frac{1}{2} \sum_{\Gamma, nik} C(\Gamma_i^{nk}) e_{\lambda}(\Gamma_i^n) e_{\lambda}(\Gamma_i^k), \qquad (115)$$

where indices *n*, *k* are numbering similar representations Γ_i . The corresponding combinations of deformation tensor components and elastic constants, as well as compatibility relations for factor-groups and point symmetry groups of lanthanide ions are given in table 8. According to the results of measurements of doublet state splittings and singlet shifts in the ground and excited multiplets of Tm^{3+} ion at uniaxial pressure of the crystals YVO₄: Tm^{3+} (Vinokurov et al. 1988b), LiYF₄: Tm^{3+} (Vinokurov et al. 1986), LiYF₄: Er^{3+} (Vinokurov et al. 1988a), LiLuF₄: Tm^{3+} and LiTmF₄ (Vinokurov et al. 1988c), the complete sets of coupling-to-deformations coefficients $B^{(r)q}_{p}$ for Tm^{3+} ions, substituting Y³⁺, Lu³⁺ ions, and $B_p^{(r)q}(T)$ for the concentrated system LiTmF₄ have been established.

The magnitudes of several constants, obtained by an analysis of piezospectroscopic measurements, differ essentially from the results of calculations within the frameworks of both the exchange charge model (see tables 9 and 10) and the superposition model (Chan et al. 1984). One of the possible reasons of this distinction are the errors when estimating coupling constants (elements of the b matrix in eq. 30) for micro- and macrodeformations, which are based on rather crude models of the lattice dynamics. It is also necessary to keep in mind that spectroscopic data allow determination of only absolute values of

NONMETALLIC LANTHANIDE COMPOUNDS

			-
Irreducible representations		Strain	Elastic constant
$D_{4h}(D_{2d})$	$C_{4h}(S_4)$		
$\overline{A_g^1(\Gamma_1^1)}$	$A_g^1(\Gamma_1^1)$	e ₂₂	$C(A_{g}^{11}) = C_{33}$
$A_g^2(\Gamma_I^2)$	$A_g^2(\Gamma_1^2)$	$(1/2)(e_{x}+e_{yy})$	$C(A_g^{22}) = 2(C_{11} + C_{12}) C(A_g^{12}) = 2C_{13}$
$B_{1g}(\Gamma_3)$	$B^1_g(\Gamma^1_2)$	$(1/2)(e_{xx} - e_{yy})$	$C(B_{1g}) = C(B_{g}^{11}) = 2(C_{11} - C_{12})$
$B_{2g}(\Gamma_4)$	$B_g^2(\Gamma_2^2)$	e_{xy}	$C(B_{2g}) = C(B_{g}^{22}) = 4C_{66} C(B_{g}^{12}) = 4C_{16}$
$E_g(\Gamma_5)$	$E_g(\Gamma_{34})$	$e_1 = e_{xz}, \ e_2 = e_{yz}$	$C(E_g) = 4C_{44}$

 Table 8

 Symmetrized strains and elastic constants for crystals with zircon and scheelite structure

Table 9 Electron-deformation interaction constants in the YVO_4 :Tm³⁺ crystal (in 10³ cm⁻¹)

pq	$B_p^{(r)q}(\mathbf{B}_{1g})$		pq	$B_p^{(r)q}(\mathbf{B}_{2g})$	
	Calculations ^a	Measurements ^b		Calculations ^a	Measurements ^b
22	-13.99	-18.8	2–2	3.16	8.9
42	7.07	12.3	4–2 ·	0.122	-0.3
62	-3.45	-0.7	6–2	0.88	5.6
66	-13.28	-9.2	66	4.31	0.2

^a Results of calculations with the exchange charge model.

^b Data obtained from piezospectroscopic measurements.

 $B_p^{(r)q}(\mathbf{A}^1_{\mathbf{g}})$ $B_p^{(r)q}(\mathbf{B}_g^1)$ $B_p^{(r)q}(\mathbf{B}_g^2)$ $B_p^{(r)q}(\mathbf{A}_g^2)$ pq pq b³ b² aª b^{1 b} bl a b² b³ а а 20 0.68 0.60 -1.81-0.8922 3.60 2.31 1.80 3.59 4.03 3.40 40 0.18 0.12 0.53 0.72 2–2 4.15 1.62 1.72 -0.82-1.23-1.1060 0.09 0.11 -0.04-0.4242 -1.36 -0.77-0.61-1.82-1.52-1.31 44 2.34 2.40 2.41 1.43 4-2 6.12 3.38 3.39 1.91 0.84 0.85 4-4 1.77 3.70 1.14 0.72 62 0.25 -0.38-0.65 -0.730.11 -0.2364 0.76 0.94 1.50 -0.846–2 -0.94 -2.94 -3.12-0.71-1.29-1.526-4 0.21 1.74 1.68 -0.89 66 -1.68 -2.22 -1.80-1.84-1.68-1.14-1.97 -3.53 -2.63 -1.61 -2.40-1.286-6

 Table 10

 Constants of electron-deformation interaction in rare-earth-lithium double fluorides (in 10³ cm⁻¹)

^a a, calculated.

^b bⁱ, experimental values for LiYF₄:Er³⁺ (b¹), LiLuF₄:Tm³⁺ (b²), LiTmF₄ (b³).

linear combinations of coupling parameters for incompletely-symmetrical deformations, so further experiments are needed to prove the data of Vinokurov et al. 1986, 1988a-c.

It may be assumed that the constants $B^{(r)q}_p$ of the coupling with deformations similarly to the crystal field parameters do not change essentially along the lanthanide series, so the data obtained for isolated R-ions, substituting Y³⁺, Lu³⁺ ions, may be used in the analysis of magnetoelastic phenomena in isostructural magnetically concentrated crystals.

As seen from table 10, parameters of coupling with deformations in the basis plane of lattice differ insignificantly for diluted and concentrated crystals, however this difference is unambiguously registered in experiments. Parameters $B^{(r)}(T)$ for thulium ions in the LiTmF₄ crystal approach those for isolated Tm³⁺ ions in the LiYF₄ crystal with increasing temperature since the generalized susceptibility χ (eq. 86) tends to zero when equalizing populations of ground multiplet sublevels.

2.6. Effective spin Hamiltonians

The peculiarities of the magnetic and magnetoelastic properties of the lanthanide compounds and the cooperative behaviour of the 4f-shell multipolar moments (magnetic dipole, electric quadrupole, etc.) are most pronounced at low temperatures, as has been mentioned in sect. 2.3. If a ground state (or a group of lower sublevels) in a crystal field is separated out of the other states by a fairly large energy interval Δ , an effective Hamiltonian $\mathcal{H}_{\rm S}$ may be introduced to describe the properties of the system at temperatures $T \ll \Delta/k_{\rm B}$ in magnetic fields $H_0 \ll \Delta/g_{\rm I}\mu_{\rm B}$.

The Hamiltonian \mathcal{H}_S is obtained by the projection of the total Hamiltonian onto a small group of the lower level states. To find an explicit dependence of crystal characteristics on a magnetic field, it is necessary to take into account the mixing of different R-ion states by the Zeeman energy operator \mathcal{H}_Z . When *n* chosen states are considered, an effective Hamiltonian may generally be represented by n^2 independent operators, in particular, by spin matrices and their products for a pseudospin S = (n-1)/2. The spin Hamiltonian structure may be derived either from symmetry considerations – operator \mathcal{H}_S must be an invariant of the point symmetry group of a lanthanide ion, and it must not contain terms changing the sign with time inversion – or by use of the perturbation theory. The main advantage of using the spin Hamiltonian formalism is the possibility to present thermodynamic and kinetic characteristics of lanthanide compounds in an analytical form, and the main drawback is that it appears impossible to compare directly the experimentally obtained parameters of Hamiltonians of different lanthanide ions even in the same crystal matrix, since the relations between these parameters and constants of the electron-phonon and electron-deformation interactions are unique for each lanthanide ion.

For a doublet ground state of an ion (it may be the Kramers doublet, the non-Kramers doublet or two states divided by a small interval δ_0), an effective Hamiltonian may be written as a linear combination of S_x , S_y , S_z operators ($S = \frac{1}{2}$). In general, the Kramers doublet is split at an arbitrary orientation of an applied magnetic field, and the corresponding effective spin Hamiltonian is

$$\mathcal{H}_{\rm S} = g_{\alpha\beta}\mu_{\rm B}H_{0\alpha}^{(c)}S_{\beta} + \mu_{\rm B}G_{\alpha\beta\gamma\delta}H_{0\alpha}^{(c)}S_{\beta}E_{\gamma\delta} + \cdots - \frac{\upsilon}{2n}H_{0\alpha}^{(c)}H_{0\beta}^{(c)}(\chi_{\alpha\beta}^{(0)} + \chi_{\alpha\beta,\gamma\delta}^{(0)}E_{\gamma\delta} + \cdots), \qquad (116)$$

where the first term is the projection of \mathcal{H}_Z , $H_0^{(c)}$ being an applied field in the crystallographic coordinate system; the second term is a projection of the electron-deformation interaction, linear on finite deformations, and the last term corresponds to the doublet shift in a magnetic field, due to the temperature-independent Van Vleck susceptibility $\chi_{\alpha\beta}^{(0)}$ (see eq. 86; more details on the VV susceptibility are given below in sect. 3) and its derivatives $\chi_{\alpha\beta,\gamma\delta}^{(0)}$ along the deformation tensor components. The components of the g-tensor are as follows:

$$g_{\alpha z} = 2g_J \langle + |J_{\alpha}| + \rangle, \qquad g_{\alpha x} = 2g_J \operatorname{Re} \langle + |J_{\alpha}| - \rangle, \qquad g_{\alpha y} = 2g_J \operatorname{Im} \langle + |J_{\alpha}| - \rangle,$$

where $|\pm\rangle$ are the Kramers-conjugated wave functions of a doublet. The splitting of a doublet in a magnetic field is

$$\Delta \varepsilon = (g_{\alpha\beta} g_{\gamma\beta} H_{0\alpha} H_{0\gamma})^{1/2}. \tag{117}$$

The dimensionless constants $G_{\alpha\beta\gamma\delta}$ of the spin-phonon interaction are linear functions of the parameters $B_{p,\alpha\beta}^q$. The spin-rotational interaction in the treatment of quasistatic magnetoelastic phenomena may be taken into account by representation of the magnetic field $H_0^{(c)}$ as a result of the rotation of an applied magnetic field H_0 , given in a laboratory coordinate system, by operator Ω (see eqs. 15 and 16) (Bonsall and Melcher 1976). The independent parameters of operator (116) are the coefficients at invariants composed of bilinear forms $\{H_{0\alpha}^{(c)}, S_{\beta}\}_{\lambda}(\Gamma_i^j)$ and linear combinations of tensors $E_{\alpha\beta}$, $H_{0\alpha}^{(c)}H_{0\beta}^{(c)}$, corresponding to irreducible representations of the point symmetry group. For example we present the spin Hamiltonian for a Kramers doublet in a crystal field with the S₄ symmetry (LiErF₄, LiDyF₄ crystals; see tables 6 and 8):

$$\begin{aligned} \mathcal{H}_{S} &= \mu_{B} \Big\{ g_{\parallel} H_{z}^{(c)} S_{z} + g'_{\perp} (H_{x}^{(c)} S_{x} + H_{y}^{(c)} S_{y}) + g''_{\perp} (H_{y}^{(c)} S_{x} - H_{x}^{(c)} S_{y}) \\ &+ \Big[G_{11}(\Gamma_{1}) e(\Gamma_{1}^{1}) + G_{12}(\Gamma_{1}) e(\Gamma_{1}^{2}) \Big] H_{z}^{(c)} S_{z} \\ &+ \Big[G'_{21}(\Gamma_{1}) e(\Gamma_{1}^{1}) + G'_{22}(\Gamma_{1}) e(\Gamma_{1}^{2}) \Big] \left(H_{x}^{(c)} S_{x} + H_{y}^{(c)} S_{y} \right) \\ &+ \Big[G''_{21}(\Gamma_{1}) e(\Gamma_{1}^{1}) + G''_{22}(\Gamma_{1}) e(\Gamma_{1}^{2}) \Big] \left(H_{y}^{(c)} S_{x} - H_{x}^{(c)} S_{y} \right) \\ &+ \Big[G_{11}(\Gamma_{2}) e(\Gamma_{2}^{1}) + G_{12}(\Gamma_{2}) e(\Gamma_{2}^{2}) \Big] \left(H_{x}^{(c)} S_{x} - H_{y}^{(c)} S_{y} \right) \\ &+ \Big[G_{21}(\Gamma_{2}) e(\Gamma_{2}^{1}) + G_{22}(\Gamma_{2}) e(\Gamma_{2}^{2}) \Big] \left(H_{x}^{(c)} S_{y} + H_{y}^{(c)} S_{x} \right) \\ &+ G(\Gamma_{34}) S_{z} (H_{x}^{(c)} e_{xz} + H_{y}^{(c)} e_{yz}) + G'(\Gamma_{34}) (S_{x} e_{xz} + S_{y} e_{yz}) H_{z}^{(c)} \\ &+ G''(\Gamma_{34}) (S_{x} e_{yz} - S_{y} e_{xz}) H_{z}^{(c)} + \cdots \Big\}. \end{aligned}$$

In eq. (118) only terms linear in deformation tensor components are taken into account, and 13 constants $G_{ij}(\Gamma)$ instead of 42 independent parameters $B_{p,\lambda}^q(\Gamma_i^j)$ of electron– deformation interaction are necessary to determine the energy of a doublet in a deformed lattice. The doublet splitting (117) in a magnetic field depends only on the absolute value of the quantity $g'_{\perp} + ig''_{\perp} = 2g_J \langle + |J_x| - \rangle$, and by a certain rotation of the coordinate system around the z-axis it is possible to exclude the terms of eq. (118) which contain $(H_y^{(c)}S_x - H_x^{(c)}S_y)$. The Zeeman energy for axial symmetry is usually as follows

$$\mathcal{H}_{Z} = g_{\parallel} \mu_{B} S_{z} H_{0z} + g_{\perp} \mu_{B} (S_{x} H_{0x} + S_{y} H_{0y})$$
(119)

where $g_{\perp} = |g'_{\perp} + ig''_{\perp}|$, and the number of constants is reduced to 11.

The energy of two-particle interactions may also be written with pseudospin operators:

$$\mathcal{H}_{ij} = K_{\alpha\beta}(ij) S_{\alpha i} S_{\beta j}.$$
(120)

Separating out the contribution of the dipole-dipole interactions, we have

$$K_{\alpha\beta}(ij) = K_{\alpha\beta}^{\mathbf{d}-\mathbf{d}}(ij) + J_{\alpha\beta}(ij), \tag{121}$$

where

$$K_{\alpha\beta}^{\rm d-d}(ij) = \left(\frac{\mu_{\rm B}^2 g_{\gamma\alpha} g_{\delta\beta}}{r^3}\right) \left(\delta_{\gamma\delta} - \frac{3x_{\gamma} x_{\delta}}{r^2}\right),\tag{122}$$

with *r* the vector connecting two ions, and parameters $J_{\alpha\beta}(ij)$ corresponding to exchange interactions.

Eu³⁺, Gd³⁺, Tb⁴⁺ ions have a half-filled 4f-shell with zero total orbital moment and spin $S = \frac{7}{2}$ in the ground state. The pure spin magnetic moment of *S*-ions is represented by an operator $\mu_S = g\mu_B S$ with the *g*-value close to 2. The exchange interaction of *S*-ions is supposed to be isotropic and is presented in the Heisenberg form:

$$J_{\alpha\beta}(ij) = J(ij) \,\delta_{\alpha\beta}$$

The projection of the operator \mathcal{H}_Z (21) onto the quasidoublet or the non-Kramers doublet ($\delta_0 = 0$) may be presented by the effective Hamiltonian (Griffiths 1963)

$$\mathcal{H}_{\rm S} = \delta_0 S_x + g_{\parallel} \mu_{\rm B} (\boldsymbol{H}_0 \boldsymbol{\mu}) S_z, \tag{123}$$

where $S_z = \pm \frac{1}{2}$ and μ is the unit vector of an ionic magnetic moment attached to the doublet (quasidoublet). In an axial crystal field vector μ is directed along the symmetry axis. In a coordinate system with the z-axis along μ the magnetic dipole-dipole interaction is represented by an operator

$$H_{ij}^{d-d} = K_{zz}^{d-d} S_{zi} S_{zj}, \qquad K_{zz}^{d-d} = \left(\frac{\mu_{\rm B}^2 g_{\parallel}^2}{r^3}\right) \left(1 - \frac{3z^2}{r^2}\right).$$
(124)

Parameters $J_{\alpha\beta}(ij)$ define not only the projections of the exchange interaction, but also the corresponding contributions of electric multipole interactions and the interaction via the phonon field. If vector r is parallel to the symmetry axis, the interaction operator for the pair of ions with non-Kramers doublets as ground states is equal to

$$H_{ij} = (K_{zz}^{d-d} + J_{\parallel}) S_{zi} S_{zj} + J_{\perp} (S_{xi} S_{xj} + S_{yi} S_{yj}).$$
(125)

The projection of the operator of the electron-deformation interaction on a non-Kramers doublet (quasidoublet) may contain invariants of the point symmetry group linear in pseudospin and independent on a magnetic field along with the terms similar to those in eq. (118).

In dielectric lanthanide compounds the direct exchange interaction between the Rions is not effective; the exchange is realized by means of ligands (superexchange). Some information on the magnitudes of effective exchange interaction parameters may be obtained from measurements of temperature dependences of the magnetic susceptibility and heat capacity (Catanese et al. 1973), from EPR and optical investigations of impurity pair centers in isomorphic compounds of lanthanum, yttrium, and lutetium (Baker 1971), and from optical and EPR spectra of impurity R-ions in magnetically ordered phases of lanthanide compounds (Bleaney 1991, Hawkes and Leask 1972). Parameters of the exchange interaction may be determined by comparing the results of calculations within the molecular field approximation with the data obtained from the phase diagrams (Laugsch et al. 1975). In a paper by Cone and Wolf (1978) a complete set of exchange interaction parameters is found for the Er³⁺ ion in a Tb(OH)₃ crystal by analysis of the Er^{3+} ion optical spectrum in a magnetically ordered phase, and the existence of an essentially anisotropic exchange field was established. The dependence of exchange integrals on interionic distance may be investigated by EPR of pair spectra under pressure; for example, Hutchings et al. (1968) obtained estimates $d \ln J/d \ln r = -13 \pm 4$ for the nearest and -22 ± 6 for the next-nearest Gd pairs in LaCl₃.

Estimates of exchange integrals according to different measurement data depend critically on the *g*-values used for calculation of magnetic dipole–dipole interactions. The *g*-values calculated within the framework of the crystal field theories usually differ from the experimental results (EPR, magnetization) by up to 10%. This difference may be due to the covalency of lanthanide ion–ligand bonds (Abragam and Bleaney 1970) and to the vibronic reduction effects (Ham 1965).

The values of interionic interaction parameters, obtained from the spectral, calorimetric, and magnetic investigations of different lanthanide compounds, are given in table 11. The relative interionic positions are specified by the vectors \mathbf{r}_{ij} in the crystallographic coordinate systems.

Comparison of the dipole–dipole coupling parameters and the effective exchange integrals shows that there are some ideal model systems among the lanthanide compounds for examining the theoretical mechanisms of electronic orbital ordering. The gadolinium compounds correspond to the Heisenberg model with the finite interaction radius; in this case the role of dipole–dipole interaction is not great. On the other hand, in rareearth ethylsulfates (RES), bromates [R(BrO₃)₃·9H₂O] and trifluoromethane sulfonates (RTFMS) of terbium, holmium, dysprosium, and erbium the magnetic ordering is possible

Table 11Constants of dipole-dipole and nondipole interactions in the lanthanide compounds $(J_{cf}(\mathbf{r}_{ij}) = J_{zz}(ij) - \frac{1}{3} \operatorname{Sp} \mathbf{J}(ij),$ z-axis is parallel to the spontaneous magnetic moment, initial splittings δ_0 for the non-Kramers doublets are given)

Compound	g-factors	r _{ij}	r _{ij} (Å)	K ^{dd} _{zz} (ij)/K	J _{zz} (ij)/K	Ref.
Pr(CF ₃ SO ₃) ₃ :9H ₂ O	$g_{\parallel} = 1.74$	(001)	7.46	-0.009	$J_{\parallel} = -0.081$	1
	n				$J_{\perp} = 0.704$	
		$(\frac{1}{2} - \frac{1}{6}\sqrt{3} \frac{1}{2})$	8.85	0.0013	$J_{\rm ef} = 0.33$	
$Pr(C_2H_5SO_4)_3:9H_2O$	$g_{\parallel} = 1.53$	(001)	7.12	-0.0081	$J_{\parallel} = -0.0024$	2
					$J_{\perp} = 0.76$	
$Tb(C_2H_5SO_4)_3:9H_2O$	$g_{\parallel} = 17.82$	(001)	7.04	-1.14	0.0244	3
$\delta_0 = 0.56 \text{ K}$						
CeBr ₃	$g_{\parallel} = 4.07$	(001)	4.44	-0.235	$J_{\parallel} = 0.65$	4
					$J_{\perp} = -0.06$	
CeCl ₃	$g_{\parallel} = 4.04$	(001)	4.315	-0.253	$J_{\parallel} = 0.60$	4
	$g_{\perp} = 0.17$				$J_{\perp} = 0.04$	
PrCl ₃	$g_{\parallel} = 1.031$	(001)	4.27	-0.017	$J_{\parallel} = 0.11 \pm 0.14$	5
					$J_{\perp} = 2.85$	
NdCl ₃	$g_{\parallel} = 4.40$	(001)	4.24	-0.31	$J_{\parallel} = -0.27$	6
	$g_{\perp} = 1.56$				$J_{\perp} = -1.4$	
GdCl ₃	g = 1.992	(001)	4.105	-0.072	0.088	4
		$(\frac{1}{2} - \frac{1}{6}\sqrt{3} \frac{1}{2})$	4.72	0.01	-0.090	
Pr(OH) ₃	$g_{\parallel} = 1.4$	(001)	3.77	-0.046	$J_{\perp} = 5.5$	7
Nd(OH) ₃	$g_{\parallel} = 3.63$	(001)	3.52	-0.376	$J_{\parallel} = 0.1 \pm 0.1$	8
	$g_{\perp} = 1.95$				$J_{\perp} = 3.6 \pm 0.4$	
		$(\frac{1}{2} - \frac{1}{6}\sqrt{3} \frac{1}{2})$	4.02	0.054	$J_{\rm ef} = 1.4 \pm 0.2$	
Gd(OH) ₃	g = 1.992	(001)	3.61	-0.106	$0.180 {\pm} 0.005$	9
		$(\frac{1}{2} - \frac{1}{6}\sqrt{3} \frac{1}{2})$	4.06	0.015	$-0.017 {\pm} 0.005$	
		(100)	6.30	0.010	$0.004 {\pm} 0.005$	
Tb(OH) ₃ $\delta_0 = 0.43$ K	$g_{\parallel} = 17.8$	(001)	3.57	-8.73	6.6	10
		$(\frac{1}{2} - \frac{1}{6}\sqrt{3} \frac{1}{2})$	4.04	1.28	-1.72	
		(100)	6.28	0.80	0.28	
$LiTbF_4 \delta_0 = 1.3 K$	$g_{\parallel} = 17.85$	$(\frac{1}{2}0\frac{1}{4})$	3.755	-2.10	$0.52 {\pm} 0.18$	11
		(100)	5.18	1.40	-0.10 ± 0.2	
LiHoF ₄	$g_{\parallel} = 13.7$	$(\frac{1}{2}0\frac{1}{4})$	3.732	-1.22	0.82	12
					0.68	13
		(100)	5.175	0.82	0.04	
LiErF ₄	$g_{\parallel} = 3.7$	$(\frac{1}{2}0\frac{1}{4})$	3.716	0.25 ª	0.62	12
	$g_{\perp} = 8.6$				-0.20	13
GdVO ₄	g=2	$(\frac{1}{2}0\frac{1}{4})$	3.94	0.021	0.120	14
GdAsO4	g = 1.992	$(\frac{1}{2}0\frac{1}{4})$	3.90	0.021	0.070	15

continued on next page

Compound	g-factors	r _{ij}	r _{ij} (Å)	$K^{dd}_{zz}(ij)/\mathrm{K}$	J _{zz} (ij)/K	Ref.
DyPO ₄	$g_{\parallel} \approx 19.5$ $g_{\perp} = 0.5$	$\left(\frac{1}{2}0\frac{1}{4}\right)$	3.775	2.28	3.04	16
HoPO₄	$g_{\parallel} = 16.96$	$(\frac{1}{2}0\frac{1}{4})$	3.761	1.755	1.14	17
					-0.604	18
		$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	5.73	0.162	0.09	
		$(0\frac{1}{2}\frac{3}{4})$	5.69	-0.885	1.95	
HoAsO₄	$g_{\parallel} = 15.3$	$(\frac{1}{2}0\frac{1}{4})$	3.865	1.269	0.394	14
	"	2 .			-0.804	18
		$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	5.90	0.101	0.186	
		$(0\frac{1}{2}\frac{3}{4})$	5.91	-0.662	1.114	
$DyVO_4, T < T_D$	$g_a = 19 \pm 0.5$	$(\frac{1}{2}0\frac{1}{4})$	3.90	$-5.74{\pm}0.4$	-0.35 ± 0.4	19
	$g_h = 0$	$\left(0\frac{1}{2}-\frac{1}{4}\right)$	3.90	$3.80{\pm}0.4$	1.75±0.4	
	$g_{c} = 0.5$	× 2 +/				
$DyAsO_4, T < T_D$	$g_a = 18.9 \pm 0.1$	$(\frac{1}{2}0\frac{1}{4})$	3.87	-5.13 ± 0.3	1.92 ± 0.3	19
	$g_h = 0$	$(0\frac{1}{2}-\frac{1}{4})$	3.87	3.40±0.3	-0.2 ± 0.3	
	$g_c < 1.2$	· 2 4/				
TbVO ₄ , $T < T_{\rm D}$,	$g_{\parallel} = 16.5$	$(\frac{1}{2}0\frac{1}{4})$	3.922	-0.72	2.06	20
$\delta_0 = 1.3 \text{ K}$	$\mu = [110]$	12 47				
$\dot{TbAsO_4}, T < T_D$	$g_{\parallel} = 17.4$	$(\frac{1}{2}0\frac{1}{4})$	3.89	-0.81	2.17	20
$\delta_0 = 0.86 \text{ K}$	$\mu = [110]$	12 47				
Tb ₂ O ₂ SO ₄	$g_{a} = 13.0 \pm 0.5$	$\left(-\frac{1}{2}-\frac{1}{4},\frac{1}{4}\right)$	3.5	4.12±1.16	21.9 ± 1.16	21
$\delta_0 < 1.45 \text{ K}$	$g_{h} = \pm 12.1 \pm 0.5$	$\left(\frac{1}{2} - \frac{1}{4} + \frac{1}{4}\right)$	3.5	-4.35 ± 0.87	16.87±0.87	
0	$g_c = \pm 1.3 \pm 0.4$	$(\pm \frac{1}{2}, \frac{1}{4}, \frac{1}{6})$	3.5	-0.23 ± 0.87	-3.36 ± 0.87	
	51	$(0\pm\frac{1}{2}0)$	4.0	-4.29±1.16	5.27 ± 1.16	
		(±100)	4.1	$-1.68 {\pm} 0.87$	$1.68 {\pm} 0.87$	
Dv ₂ O ₂ SO ₄	$g_{a} = 18.2$	$(\pm \frac{1}{2} \pm \frac{1}{4} \frac{1}{4})$	3.5	-0.58 ± 0.35	14.9 ± 0.35	21
52 2 4	$g_{\rm h} < 1.5$	$(0\pm\frac{1}{2}0)$	4.0	3.36 ± 0.40	1.62 ± 0.40	22
	$g_{c} < 1.5$	(± 100)	4.1	-6.43 ± 2.03	4.06 ± 2.03	
Ho ₂ O ₂ SO ₄	$g_{a} = 18.7 \pm 0.1$	$(\pm \frac{1}{2} \pm \frac{1}{2} \pm \frac{1}{2})$	3.5	-0.58 ± 0.35	-6.03 ± 0.35	21
$\delta_0 = 3.8 \pm 0.5 \text{ K}$	g, <1.5	$(0\pm\frac{1}{2}0)$	4.0	3.25±0.35	0.58±0.35	-
•	$g_c = 3.2 \pm 0.5$	(±100)	4.1	6.03±0.35	0.98±0.35	
GdAlO ₃	g=2	(nn)	3.85	-0.088	0.134	23

Table 11, continued

continued on next page

only due to magnetic dipole-dipole interactions. The non-Kramers ion compounds and a number of dysprosium compounds (e.g., DyES) represent Ising systems, and magnetic

Table 11, notes					
^a Average per ion.					
References					
(1) Petasis et al. (1993)	(9) Skjeltorp et al. (1973)	(17) Cooke et al. (1973)			
(2) Folinsbee et al. (1977a)	(10) Catanese et al. (1973)	(18) Laugsch et al. (1975)			
(3) Anderson et al. (1971)	(11) Holmes et al. (1975)	(19) Kasten (1980)			
(4) Skjeltorp (1978)	(12) Beauvillain et al. (1978a)	(20) Gehring et al. (1976a)			
(5) Harrison et al. (1976)	(13) Mennenga et al. (1984a)	(21) Kahle and Kasten (1983)			
(6) Skjeltorp (1977)	(14) Becher et al. (1975)	(22) Hulsing and Kasten (1979)			
(7) Folinsbee et al. (1977b)	(15) Colwell et al. (1971)	(23) Cashion et al. (1970)			
(8) Ellingsen et al. (1982)	(16) Wright et al. (1971)				

properties of crystals with $g_{\parallel} \ll g_{\perp}$ in the ground state may be compared to those of the XY model. Characteristics of the thermodynamic properties in magnetically ordered states and the critical behaviour of lanthanide compounds will be considered in greater detail in sect. 4.

3. Van Vleck paramagnets

3.1. Magnetic susceptibility

The distinctive features of Van Vleck paramagnets are the relatively large electronic magnetic moment induced by an applied field and the "enhanced" nuclear magnetism of lanthanide ions. Yet molecular magnetic fields in these systems are usually much less than the external ones, so in calculations of magnetization it is quite reasonable to confine consideration to a single-ionic approximation. The Hamiltonian of a single Van Vleck ion has the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \qquad \mathcal{H}' = \mathcal{H}_Z + \mathcal{H}_{\rm hf} + \mathcal{H}_{\rm I} + \mathcal{H}_{\rm O}, \tag{126}$$

where the crystal field energy (\mathcal{H}_0) , electron Zeeman (\mathcal{H}_Z) , nuclear Zeeman (\mathcal{H}_I) , hyperfine (\mathcal{H}_{hf}) , and nuclear quadrupolar (\mathcal{H}_Q) interactions are defined by eqs. (5), (21), (24), (22), and (23) and (25), respectively.

To illustrate the relative values of the terms in eq. (126), a model electron-nuclear spectrum of a Van Vleck ion, embracing the two lowest electron levels and resembling the spectra of Tm^{3+} ions in TmES and LiTmF₄ crystals, is drawn in fig. 8. In the absence of the perturbation \mathcal{H}' the levels are a ground-state singlet and a doublet with an excitation energy Δ (\approx 32 cm⁻¹ for Tm³⁺ ions in TmES and LiTmF₄). In an applied field H_0 the doublet is split by the amount Ω ; a small initial splitting Ω_0 due to crystal field distortions is not eliminated. Each state with regard to a nuclear spin $I = \frac{1}{2}$ is twofold degenerate, and inclusion of hyperfine and nuclear Zeeman interactions results in further splitting of electron-nuclear states.



The equilibrium magnetization per unit volume is represented as a sum of electronic and nuclear terms:

$$\boldsymbol{M}_{\text{total}} = \boldsymbol{M} + \boldsymbol{m} = \frac{n}{v} [-g_{J} \mu_{B} \operatorname{Sp}(\rho \boldsymbol{J}) + \gamma_{I} \hbar \operatorname{Sp}(\rho \boldsymbol{I})], \qquad (127)$$

where ρ is the density matrix:

$$\rho = \frac{\exp(-\mathcal{H}/k_{\rm B}T)}{\operatorname{Sp}\exp(-\mathcal{H}/k_{\rm B}T)}.$$
(128)

The electronic term in the first approximation on $\mathcal{H}'/k_{\rm B}T$ is equal to

$$\boldsymbol{M}_{\boldsymbol{H}}^{(1)} = \boldsymbol{\chi}^{(T)} \boldsymbol{H}_{0}, \tag{129}$$

where the temperature-dependent susceptibility tensor is defined by the Van Vleck formula (Van Vleck 1932) which is a special case of eq. (86) for $\hat{A} = \hat{B} = J$ and $\mathcal{H}_Z = 0$. For systems with a nonmagnetic ground state the formula is applicable at arbitrary low temperatures, when only the ground electronic level is populated; for a singlet ground level in this case we obtain the Van Vleck susceptibility independent of temperature:

$$\chi_{\alpha\beta}^{(0)} = \frac{n}{v} (g_{\mathrm{J}}\mu_{\mathrm{B}})^2 T_{\alpha\beta}, \qquad T_{\alpha\beta} = \left\langle 0 \left| J_{\alpha}C_0 J_{\beta} + J_{\beta}C_0 J_{\alpha} \right| 0 \right\rangle,$$

$$C_0 = \sum_{m} (E_m - E_0)^{-1} \left| m \right\rangle \left\langle m \right|.$$
(130)

In nuclear magnetization the second-order term $m^{(2)}$ may prevail, and the resulting magnetization corresponds to an "enhanced" external magnetic field:

$$\boldsymbol{m} = \boldsymbol{m}^{(1)} + \boldsymbol{m}^{(2)} = \frac{\gamma_I^2 \hbar^2 I(I+1)}{3k_{\rm B}T} \left(\frac{n}{v} + \frac{A_{\rm J}}{g_{\rm J} \mu_{\rm B} \gamma_I \hbar} \boldsymbol{\chi}^{(T)} \right) \cdot \boldsymbol{H}_0.$$
(131)

The contribution to M in the second order in perturbation \mathcal{H}' represents magnetization induced by a nuclear moment on an electronic shell, and its value coincides with $m^{(2)}$:

$$\boldsymbol{M}_{I}^{(2)} = \frac{v}{n} \frac{A_{\mathrm{J}}}{g_{\mathrm{J}} \mu_{\mathrm{B}} \gamma_{I} \hbar} \boldsymbol{\chi}^{(T)} \cdot \boldsymbol{m}^{(1)}.$$
(132)

The main third-order contributions are additions to $M_{\rm H}$ which are nonlinear in H_0 and an "enhanced" contribution of the nuclear moment to electronic magnetization. The latter is especially significant at very low temperatures, $|\mathcal{H}'| \ge k_{\rm B}T$. Under these conditions the calculation of the magnetization is simplified since only the nuclear sublevels of the ground electronic singlet are populated. The energy and eigenfunctions of the nuclear multiplet are calculated in the following approximate manner. The electronic state is written down to second order in the perturbation:

$$\left|\widetilde{O}\right\rangle = \left|0\right\rangle - P_{\alpha}C_{0}J_{\alpha}\left|0\right\rangle - \frac{1}{2}\left|0\right\rangle P_{\alpha}P_{\beta}\left\langle0\right|J_{\alpha}C_{0}^{2}J_{\beta}\left|0\right\rangle + P_{\alpha}P_{\beta}C_{0}J_{\alpha}C_{0}J_{\beta}\left|0\right\rangle,$$
(133)

where $P_{\alpha} = g_J \mu_B H_{0\alpha} + A_J I_{\alpha}$. Nuclear spin moments in this expression operate on nuclear states when the total electron-nuclear wave functions are written down. The energy of the system in the ground electronic state in this approximation represents an effective nuclear spin Hamiltonian:

$$\left\langle \widetilde{\mathbf{O}} \left| \mathcal{H}_{0} + \mathcal{H}' \right| \widetilde{\mathbf{O}} \right\rangle = E_{0} - \gamma_{I} \hbar \left[\delta_{\alpha\beta} + \frac{A_{J}g_{J}\mu_{B}}{\gamma_{I}\hbar} T_{\alpha\beta} \right] H_{0\alpha}I_{\beta} + \left[\left\langle 0 \left| q_{\alpha\beta}(J) \right| 0 \right\rangle - \frac{1}{2}A_{J}^{2}T_{\alpha\beta} \right] \left[I_{\alpha}I_{\beta} - \frac{1}{3}I(I+1) \right],$$
(134)

where the tensor $q_{\alpha\beta}$ is readily obtained from eqs. (23) and (25). An effective nuclear Zeeman Hamiltonian can be rewritten in the following forms which are often mentioned in the literature:

$$\mathcal{H}_{\mathrm{IZ}}^{\mathrm{eff}} = -\gamma_{I}\hbar H_{0} \left[1 + \left(\frac{A_{\mathrm{J}}}{\gamma_{I}\hbar g_{\mathrm{J}}\mu_{\mathrm{B}}} \right) \frac{v}{n} \chi^{(0)} \right] I = -\gamma_{I}\hbar H_{0}(1+\alpha) \cdot I$$

$$= -\hbar H_{0} \cdot \gamma \cdot I = -\gamma_{I}\hbar H' \cdot I.$$
(135)

Here α is the paramagnetic shift tensor, γ is the effective gyromagnetic ratio, and H' is the enhanced magnetic field. The quadrupolar energy in eq. (134) includes a "pseudoquadrupolar" term due to the hyperfine interaction \mathcal{H}_{hf} . A nuclear spin Hamiltonian in the main axes of γ and q tensors is written in the form

$$\mathcal{H}_{I} = -\hbar(\gamma_{x}H_{0x}I_{x} + \gamma_{y}H_{0y}I_{y} + \gamma_{z}H_{0z}I_{z}) + q\left\{ \left[I_{z'}^{2} - \frac{1}{3}I(I+1) \right] + \eta(I_{x'}^{2} - I_{y'}^{2}) \right\}.$$
(136)

At axial symmetry of the R-ion position in a crystal, the main axes of those tensors coincide, $\gamma_x = \gamma_y = \gamma_{\perp}$, $\gamma_z = \gamma_{\parallel}$ (z denotes a principal crystal axis), so the nuclear spin Hamiltonian can be written as

$$\mathcal{H}_{I} = -\gamma_{\parallel} \hbar H_{0z} I_{z} - \gamma_{\perp} \hbar (H_{0x} I_{x} + H_{0y} I_{y}) + q [I_{z}^{2} - \frac{1}{3} I(I+1)].$$
(137)

As temperature increases, rapid jumps between the 4f-shell levels occur in the crystal, and the nucleus is subjected to momentary influence of different hyperfine fields created

348

by thermally excited electrons. As a result the nuclear spin Hamiltonian parameters gain a temperature dependence defined by the fluctuation correlation time; the temperaturedependent resonance line shift arises, examples of which we shall consider in sect. 3.3.1.

Returning to the magnetization at low temperatures we shall consider in detail the case $I = \frac{1}{2}$. The splitting of the nuclear doublet at an arbitrary orientation of an applied magnetic field is equal to $\hbar\omega_0 = \gamma_I \hbar H'$, $H' = (H'^2)^{1/2}$, and the stationary electron–nuclear states can be written down as follows

$$\widetilde{O1} \rangle = \left| \widetilde{O} \right\rangle \left\{ \cos(\frac{1}{2}\theta') \left| +\frac{1}{2} \right\rangle + \sin(\frac{1}{2}\theta') e^{i\varphi'} \left| -\frac{1}{2} \right\rangle \right\},$$

$$\widetilde{O2} \rangle = \left| \widetilde{O} \right\rangle \left\{ -\sin(\frac{1}{2}\theta') e^{-i\varphi'} \left| +\frac{1}{2} \right\rangle + \cos(\frac{1}{2}\theta') \left| -\frac{1}{2} \right\rangle \right\},$$

$$(138)$$

where θ' and φ' are the polar angles of the vector H'; in the case of axial symmetry one has $\cos \theta' = (\gamma_{\parallel}/\gamma) \cos \theta$, $\varphi' = \varphi$, $\gamma^2 = \gamma_{\parallel}^2 \cos^2 \theta + \gamma_{\perp}^2 \sin^2 \theta$, (θ, φ) being the polar angles of an applied field H_0 in the main-axes coordinate system. Entirely neglecting the population of other states than the electron-nuclear states of eq. (138) we obtain the following expressions for the magnetization:

$$\boldsymbol{m} = \frac{n}{2\nu} \gamma_I \hbar \left[1 + \frac{A_{\rm J} g_{\rm J} \mu_{\rm B}}{\gamma_I \hbar} \boldsymbol{T} \right] \left(\frac{\boldsymbol{H}_0}{\boldsymbol{H}'} \right) \tanh \left(\frac{\gamma_I \hbar \boldsymbol{H}'}{2k_{\rm B} T} \right), \tag{139}$$

$$M = M_H + M_I,$$

$$M_H = \frac{n}{\nu} (g_J \mu_B)^2 T H_0 = \chi^{(0)} H_0, \qquad M_I = \left(\frac{A_J g_J \mu_B}{\gamma_I \hbar}\right) T m.$$
(140)

For $k_B T \gg \hbar \omega_0$, as was to be expected, *m* coincides with eq. (132). The direction of *m* (which according to eq. (136) is also the quantization axis *Z* of the nuclear spin and the direction of the effective "enhanced" field H') is in general different from the direction of the Van Vleck magnetization M_H . Usually M_H exceeds all other terms by far; however, as mentioned by Bleaney (1980), at ultralow temperatures when the nuclear spin system



Fig. 9. Magnetic moment components of the ¹⁶⁹Tm³⁺ ion in a TmES crystal; the external magnetic field H_0 forms an angle $\theta = 1^\circ$ with the *c*-axis of the crystal; the effective (enhanced) field at the nucleus H' and the nuclear moment m_1 form an angle $\theta' = 44^\circ$; the electron (Van Vleck) moment $M_{\rm H}$, an angle of 74°; the electron-nuclear moment M_1 , an angle of 89°.

is appreciably polarized even by a weak field, the term M_I may prevail. For crystals with axial symmetry all the components of the magnetization lie in the plane with the symmetry axis c and the applied magnetic field direction. Figure 9 illustrates the "fan" of these components for TmES when the external field is oriented at an angle of 1° to the c-axis.

3.2. Magnetoelastic properties and nonlinear magnetic susceptibility

Magnetoelastic phenomena are manifested in VV paramagnets at helium temperatures and applied magnetic fields up to several tens kOe even more clearly than in normal paramagnets, despite the essentially smaller changes of energies of the populated states. In this subsection we shall consider the forced magnetostriction (parastriction), the changes of elastic constants induced by a magnetic field and the inverse effect of a deformed lattice on magnetization of VV paramagnets for specific examples of the LiTmF₄, HoVO₄ and TmPO₄ crystals.

The structure and elastic properties of the lanthanide double fluorides LiRF₄, and phosphates RPO₄, depending on temperature and magnetic field, have been systematically studied both experimentally and theoretically from the late the seventies (Al'tshuler et al. 1985, Sokolov et al. 1991). The effectiveness of electronic subsystem coupling with the lattice in lanthanide compounds correlates with distinctions of temperature dependences of single crystal lattice parameters, elastic constants, and Young's modulus, from the corresponding dependences in isomorphic diamagnetic compounds. In particular, anomalies of a temperature expansion characterize the coupling of lanthanide ions to the full-symmetric deformations. Stresses in a tetragonal lattice, due to 4f electrons, induce the deformations (cf. eq. 99 and table 8)

$$e(A_{g}^{i}|T) = -\frac{4}{a^{2}c} \sum_{j} S(A_{g}^{ij}|T) \sum_{pq} B_{p}^{(r)q}(A_{g}^{j}|T) \left\langle O_{p}^{q} \right\rangle_{0}.$$
 (141)

Relative changes of lattice parameters $\Delta c(T)/c$ and $\Delta a(T)/a$ at helium to room temperatures for the LiRF₄ and RPO₄ crystals have been measured with X-ray methods by Abdulsabirov et al. (1993) and Sokolov et al. (1991, 1992a). They have found clear anomalies of the thermal expansion of lanthanide compounds in comparison with the temperature change of the lattice parameters a, c of the diamagnetic crystals LiLuF₄ and YPO₄. At T = 4.2 K, when only the ground levels of Tm³⁺ ions are populated (see table 5), the differences in the relative changes of the parameters a, c in the LiTmF₄ and LiLuF₄ crystals are equal to $\delta c/c = e(A_g^1) = 1.5 \times 10^{-4}$, $\delta a/a = e(A_g^2) = -4.5 \times 10^{-4}$; the corresponding differences in TmPO₄ and YPO₄ are $\delta c/c = -9 \times 10^{-4}$, $\delta a/a = 7 \times 10^{-4}$. A calculation by means of eq. (141), with the theoretical estimates of coupling constants $B_p^{(r)q}(A_g^i)$ for the LiTmF₄ crystal (table 10) and the measured elastic constants at 4.2 K (table 12), results in the values $\delta c/c = 5.4 \times 10^{-4}$, $\delta a/a = -13 \times 10^{-4}$, which correspond both by sign and order of magnitude to the experimental data.

NONMETALLIC LANTHANIDE COMPOUNDS

	LuPO ₄ ^a	LuAsO4 ª	RVO ₄ ^b	LiTmF ₄ °
$C(\mathbf{A}_{\mathbf{g}}^{11})$	382	323	320	173.4
$C(A_{\mu}^{22})$	712	606	554	362.3
$C(A_g^{12})$	230	204	200	130
$C(\mathbf{B}_{1g}) = C(\mathbf{B}_{g}^{11})$	568	502	462	126.9
$C(\mathbf{B}_{2g}) = C(\mathbf{B}_{g}^{22})$	86.8	77.6	66.0	78.8
$C(\mathbf{B}_{\mathbf{g}}^{12})$	-		-	-71.0
$C(E_{p})$	338	286	220	169.2

 Table 12

 Elastic constants of lanthanide crystals with zircon and scheelite structure (in GPa)

^a Armbruster et al. (1974).

^b Melcher (1976), Bleaney et al. (1988a), Goto et al. (1986).

^c Aukhadeev et al. (1983).

The effects of the Tm^{3+} ion interaction with A_g -strains are relatively small, which is also confirmed by the measurements of temperature dependences of acoustic wave velocities for different directions of propagation and polarizations in a LiTmF₄ crystal (Aukhadeev et al. 1981) and HoVO₄ (Goto et al. 1986) crystals, and, by comparison of the Young's modulus in polycrystalline TmPO₄, with the temperature dependence of that modulus in YPO₄ (Sokolov et al. 1991). The relative changes of the elastic constants $C(A_g^{\mu})$ for the LiTmF₄ crystal at the temperature range 4.2–30 K do not exceed 10%. The temperature dependence of Young's modulus E(T) in polycrystalline samples characterizes only the mean value of corrections to the elastic constants, conditioned by the electron-deformation interaction, and an observed anomaly of the E(T) dependence in the TmPO₄ crystal near T = 20 K is due to the deep minimum of an elastic constant C_{66} at that temperature (Harley and Manning 1978). Essential changes of elastic constants $C(B_g^{\mu})$ of the $LiTmF_4$ and HoVO₄ crystals, which define deformations in the basis plane of the lattice, have also been discovered by Aukhadeev et al. (1981) and Goto et al. (1986) in the temperature range 10-30 K. These experimental facts form the basis for inquiring into the estimates of correlations of the B_{g} -symmetry deformations in the LiTmF₄ crystal and the B_{1g} - and B_{2g} -symmetry deformations in the TmPO₄, HoVO₄ crystals.

The degree of the mutual influence of lanthanide ion electronic shells is determined by the tensor η (eqs. 77, 73). Until recently no rigorous calculations of components of η had been done. Crude estimates may be carried out, neglecting the dispersion of optical branches. Using the following equations between the constants of coupling with even (j_g) and odd (j_u) optical vibrations of the R-ions, linked with each other through an inversion,

$$B_p^q(1|0j_g) = B_p^q(2|0j_g), \qquad B_p^q(1|0j_u) = -B_p^q(2|0j_u),$$
Al'tshuler et al. (1985) have found

$$\eta_{pp'}^{qq'} = \sum_{j_{g}} \omega_{jg}^{-2}(0) B_{p}^{q}(1|0j_{g}) B_{p'}^{q'}(1|0j_{g}) - \sum_{j_{u}} \omega_{ju}^{-2}(0) B_{p}^{q}(1|0j_{u}) B_{p'}^{q'}(1|0j_{u}) - \frac{1}{N} \sum_{j_{a}q} \omega_{ja}^{-2}(q) B_{p}^{q}(1|q_{j_{a}}) B_{p'}^{q'}(1|-q_{j_{a}}).$$
(142)

The space of electronic operators O_p^q is naturally decomposed into subspaces, conforming to irreducible representations of a symmetry group of the Brillouin zone center and having the corresponding tensors $\eta(\Gamma_i)$. To calculate the quantities (142), the parameters of an electron-deformation interaction (eq. 19) are necessary; besides only coupling constants with odd optical vibrations are necessary, if acoustic vibrations are considered in the long-wave approximation. Parameters $B_p^q(1|j_{g(u)})$ are linear combinations of $B'_{p\lambda}(\Gamma_i^j)$ (eq. 112) with coefficients defining the expansion of the dynamic matrix eigenfunctions at the Γ -point in symmetrized displacements $w_{\lambda}(\Gamma_i^j)$ of the sublattices. For example, the equation for $\eta(B_{2g})$ components in crystals with zircon structure (see eq. 56) is:

$$\eta_{pp'}^{qq'}(B_{2g}) = \omega^{-2}(B_{2g}) B_{p'}^{q}(B_{2g}) B_{p'}^{'q'}(B_{2g}) - \omega^{-2}(A_{1u}) B_{p}^{'q}(A_{1u}) B_{p'}^{'q'}(A_{1u}) - \frac{\left\langle v_{ja}^{3} \right\rangle_{\Omega}}{3dv} \left\langle \frac{1}{4v_{ja}^{5}} [e_{x}(j_{a}\boldsymbol{q}_{0}) q_{0y} + e_{y}(j_{a}\boldsymbol{q}_{0}) q_{0x}]^{2} \right\rangle_{\Omega} B_{p'}^{(r)q}(B_{2g}) B_{p'}^{(r)q'}(B_{2g}),$$
(143)

where $\langle A \rangle_{\Omega} \sum_{j_a} \frac{1}{4\pi} \int A d\Omega$ is an average over the propagation directions of acoustic waves with the velocity v_{j_a} and d is the crystal density. Interactions of R-ions with four B_{1g} -vibrations and three A_{2u} -vibrations contribute to the tensor $\eta(B_{1g})$; the tensor $\eta(B_g)$ for LiRF₄ crystals contains contributions from the interaction with five B_g -symmetry and four A_u -symmetry vibrations. The numerical estimates of elements of the symmetrical matrices $\eta(B_{1g})$, $\eta(B_{2g})$ (the fourth-rank matrices) and $\eta(B_g)$ (the eighth-rank matrix) have been made within the framework of the exchange charge model by use of the results of lattice dynamic analysis for RMO₄ crystals (Pekurovskii 1987) and LiRF₄ crystals (Bumagina et al. 1981). The values of the $\eta(B_{ig})$ components have been calculated by Malkin et al. (1993) using the parameters of coupling with macroscopic deformations (table 10) as found from piezospectroscopic measurements; the indices of the matrix $\eta(B_{1g})$ correspond to the following numbering of electronic operators O_p^q : $1, O_2^2; 2, O_4^2; 3, O_6^2; 4, O_6^6$; and the operators for B_{2g} -symmetry are numbered similarly by changing the index q to -q. The results are:

	11	12	13	14	22	23	24	33	34	44
$\overline{\boldsymbol{\eta}(B_{1g})}$	-169.3	62.1	10.9	-58.7	-62.2	4.4	32.3	25.3	5.5	-22.2
$\boldsymbol{\eta}(B_{2g})$	-113.8	-5.1	-63.6	-8.5	3.30	2.8	-8.3	-36.0	-6.4	4.3

The components of the $\eta(B_g)$ tensor for LiRF₄, calculated by Al'tshuler et al. (1985) (the matrix in the basis of eight operators $O_2^{\pm 2}$, $O_4^{\pm 2}$, $O_6^{\pm 2}$, $O_6^{\pm 6}$) do not exceed 100 cm⁻¹by modulus. Tm³⁺ ions in TmPO₄ and LiTmF₄ have a similar structure of the lower energy levels of the ground multiplet (table 5): the first excited state is a doublet of energy $30 \,\mathrm{cm}^{-1}$, which effectively interacts with the B_{2g} - and B_{g} -deformations, however, it mixes with the ground state only in a magnetic field, perpendicular to the c-axis of a lattice; the second excited state is a singlet of energy $60-70 \text{ cm}^{-1}$, which makes the main contribution to the low-temperature generalized susceptibility χ_0 of the 4f-shell electron multipoles of B_g (LiTmF₄) and B_{2g} (TmPO₄) symmetries. The calculations show that at liquid helium temperatures, when only the ground singlet Γ_g is populated, it is possible to take into account its mixing with only one excited singlet Γ_e of energy Δ . In this case the generalized susceptibility may be presented as a dyad, $\chi_{0pp'}^{qq'} = A_p^q A_{p'}^{q'}$, the components of the vector A being equal to $A_p^q = (2/\Delta)^{1/2} \langle \Gamma_e | O_p^q | \Gamma_g \rangle$. Equations (93)-(95) and (103) can now be essentially simplified (Al'tshuler et al. 1985); in particular, the following expression is obtained for the elastic constants, neglecting the nonlinear electron-deformation interaction:

$$C(T) = C - \frac{n}{\nu} (1 - \tau - \tau')^{-1} B^{(r)} : \chi_0 : B^{(r)},$$
(144)

where

$$\tau = \operatorname{Sp} \boldsymbol{\chi}_0 : \boldsymbol{\eta}, \qquad \tau' = \frac{n}{\nu} \operatorname{Sp} \boldsymbol{a}^{-1} \boldsymbol{B}' : \boldsymbol{\chi}_0 : \boldsymbol{B}'.$$
(145)

The calculated relative contributions of the electronic subsystem to the elastic constants of a LiTmF₄ crystal at T = 4.2 K ($\tau = -0.29$, $\tau' = 0.16$) are -16% ($C(B_g^{11})$), -12% ($C(B_g^{22})$) and -20% ($C(B_g^{12})$), and they are consistent with the measured differences between the corresponding elastic constants of LiLuF₄ and LiTmF₄, as well as with their changes upon raising the temperature from 4.2 to 77 K (Aukhadeev et al. 1981). When the temperature is raised, the nearest excited doublet is populated and the generalized susceptibility grows; at still higher temperature and population of the Γ_e singlet, the components of the susceptibility tensor begin to decrease, which results in a specific minimum in the temperature dependences of B_g -symmetry elastic constants near T = 20 K. The calculated differences between elastic constants at 0 and 20 K, $\delta C(B_g^{11}) = 3.1$, $\delta C(B_g^{12}) = 3.4$, $\delta C(B_g^{22}) = 3.36$ GPa, agree by magnitude and sign with the measured data (Aukhadeev et al. 1981). The contributions of $\mathcal{H}_{e-1}^{(2)}$ to $C(B_g^{ij})$ at low temperatures are of the order of -1 GPa, and their absolute values decrease with increasing temperature.

The linear coupling between uniaxial strains along [100] and [110] directions in the basis plane, corresponding to different $(B_{1g} \text{ and } B_{2g})$ irreducible representations of the lattice symmetry group, is not found in crystals with the zircon structure, as opposed to the compounds with the scheelite structure. The components of tensors $\eta(B_{1g})$ and $\eta(B_{2g})$, as seen from the above calculations, are comparable in magnitude, so the primary effectiveness of certain strains are defined entirely by the value of the corresponding

generalized susceptibility, that is, by the structure of an energy spectrum of $4f^n$ -shell in the crystal field. For Tm^{3+} ions in the TmPO₄ crystal the generalized susceptibility $\chi_0(B_{1g})$ at low temperatures has essentially smaller components than $\chi_0(B_{2g})$, partly because the matrix elements of B_{1g} -symmetry operators on the wave functions of the ground and nearest excited singlet states equal zero.

The linear electron-deformation interaction always results in temperature softening of the elastic constants. However, as has been already mentioned, only one constant, $C(B_{2\alpha})$, of the TmPO₄ crystal has a characteristic temperature dependence in the range of 4-50 Kwith a deep minimum at $T \approx 20 \,\mathrm{K}$ (Harley and Manning 1978), due to the population of the lowest excited doublet, just as in the case of $LiTmF_4$. On the contrary, for Ho³⁺ ions in the HoVO₄ crystal, the components of tensors $\chi_0(B_{1g})$ and $\chi_0(B_{2g})$ are comparable in magnitude (the ground singlet is effectively mixed with the excited singlets of energies 48 and 222 cm⁻¹ by B_{1g} - and B_{2g} -symmetry perturbations, respectively), and characteristic temperature dependences with minima near 13-14 K, due to the finite population of the nearest excited doublet of the energy 21 cm⁻¹, were observed by Goto et al. (1986) for the elastic constants $C(B_{1g})$ and $C(B_{2g})$. Simple theoretical estimates of the contributions of the electronic subsystem to the elastic constants $[\Delta C \approx (-2/\nu) B^{(r)}; \chi_0; B^{(r)}]$ in accordance with eq. (95)], using the coupling parameters $B^{(r)}$ (table 10) found from piezospectroscopic investigations, give results conforming to the measurement data. At T = 4.2 K the corresponding corrections to $C(B_{1g})$ and $C(B_{2g})$ equal -18 and -4 GPa, respectively; and the depths of the minima (difference between elastic constants at 4.2 K and at 13–14 K) are 8 GPa for $C(B_{1g})$ and 0.8 GPa for $C(B_{2g})$.

It should be noted that, although the elastic constants have been measured by ultrasonic pulse-echo overlap and phase detection methods in a 10–16 MHz frequency range, the data may be interpreted within the framework of the quasistatic process theory, since in VV paramagnets the electronic relaxation rate is defined by spontaneous transitions between Stark sublevels, and the relaxation times do not exceed 10^{-10} s even at helium temperatures. Only in the presence of a nuclear magnetic moment of the lanthanide ion and cooling to temperatures of the order of 0.1 K, comparable with the hyperfine structure constant, can additional anomalies of the temperature dependence of elastic constants be revealed due to the different populations of hyperfine components of the R-ion energy spectrum. For example, the velocity of sound propagating along the *c*-axis of the LiTbF₄ ferromagnet ($T_C = 2.89$ K) has been found to decrease by 0.0009% when temperature decreases from 0.5 K down to 0.04 K (Al'tshuler et al. 1984).

The magnetostriction of nonconducting VV paramagnets is specified by strong anisotropy, and at helium temperatures in relatively small magnetic fields (20-40 kOe) it may reach an enormous value, comparable to that in lanthanide metals. Since the relaxation times in VV paramagnets are small, these compounds hold promise for microwave sound oscillators.

The first clear ideas on magnetostriction mechanisms in VV paramagnets were formulated by Al'tshuler et al. (1980), proceeding from experimental investigations of magnetoelastic phenomena in the LiTmF₄ crystal. Parastriction is determined by the ratio of the magnetic energy of a crystal to the elastic deformation energy, and it is proportional

to the product of applied magnetic field and magnetization. Since the induced magnetic moment of a VV paramagnet is proportional to the applied field, parastriction is described by the following expression (see eq. 111):

$$\frac{\Delta L}{L} = \alpha \left(T, \frac{H_0}{H_0}, \mathbf{n} \right) H_0^2 \tag{146}$$

and it is not saturated to very high values of the field strength at temperatures $T \ll \Delta/k_{\rm B}$, where Δ stands for the energy of the excited states.

The relative changes in the crystal length were measured by capacitive methods in the LiTmF₄ compound at temperatures 1.5–4.2 K and magnetic fields up to 30 kOe and in the TmPO₄ compound at 4.5–40 K and fields up to 50 kOe for directions parallel and perpendicular to an applied field [longitudinal, $(\Delta L/L)_{\parallel}$ and transverse, $(\Delta L/L)_{\perp}$ magnetostriction] (Al'tshuler et al. 1980, Bondar' et al. 1988).

A magnetic field parallel to the *c*-axis induces only full-symmetric deformations: $(\Delta L/L)_{\parallel} = e(A_g^1), (\Delta L/L)_{\perp} = e(A_g^2)$. Since at full-symmetric perturbations the ground singlet of Tm³⁺ ions is mixed only with the singlets of the same symmetry with high excitation energies, the interaction with A_g -strains is weak (as mentioned above when considering the temperature effects). Thus, in the highest applied fields available in the discussed experiments the forced deformation did not exceed 10^{-6} .

A magnetic field perpendicular to the symmetry axis (vector H_0 in (001)-plane at angle ϕ to the axis [100]), induces both full-symmetric and axial deformations in the basis plane; for LiTmF₄

$$\left(\frac{\Delta L}{L}\right)_{\parallel} = e(A_{g}^{2}) + \cos 2\phi e(B_{g}^{1}) + \sin 2\phi e(B_{g}^{2}), \quad \boldsymbol{n} \parallel \boldsymbol{H}_{0};$$

$$\left(\frac{\Delta L}{L}\right)_{\perp} = e(A_{g}^{2}) - \cos 2\phi e(B_{g}^{1}) - \sin 2\phi e(B_{g}^{2}), \quad \boldsymbol{n} \perp \boldsymbol{H}_{0}, \quad \boldsymbol{n} \perp \boldsymbol{c}_{0}$$

For TmPO₄ one must substitute B_g^1 by B_{1g} and B_g^2 by B_{2g} in these equations. The measured longitudinal and transverse strictions in the LiTmF₄ crystal are equal in magnitude (with an accuracy of 10⁻⁶) and have opposite signs, so the field $H_0 \perp [001]$ induces mainly B_g -deformations: $e(B_g^i) = (a_i \cos 2\phi + b_i \sin 2\phi)H_0^2$. The coefficients a_i and b_i are found through corrections to eigenvalues of \mathcal{H}_0 due to the perturbation $\mathcal{H}_Z + \mathcal{H}_{e-1}^{(1)}$ (of second order in \mathcal{H}_Z and linear in the deformation tensor). The dependence of the striction on the orientation of H_0 in the basal plane of a tetragonal lattice has the form of a specific four-petal rosette (B_g -deformations):

$$\left(\frac{\Delta L}{L}\right)_{\parallel} = \left\{A + B\cos[4(\varphi - \varphi_0)]\right\} H_0^2$$

where

$$A = \frac{1}{2}(a_1 + b_2), \qquad B = \frac{1}{2}[(a_1 - b_2)^2 + (a_2 + b_1)^2]^{1/2}, \qquad \arctan 4\varphi_0 = \frac{(a_2 + b_1)}{(a_1 - b_2)}.$$

The values of three independent parameters determining the magnetostriction of LiTmF₄ crystals at helium temperatures in a field $H_0 \perp [001]$ were calculated by use of the



Fig. 10. Longitudinal magnetostriction of a LiTmF₄ crystal at liquid helium temperature in the external field H_0 along the (1) [110], (2) [100] and (3) [210] directions.

measured elastic constants (table 12) and coupling constants $B^{(r)}(B_g|T)$ (table 10). The resulting values agree well with the measurements of Al'tshuler et al. (1980) (see fig. 10): A = -5.8 (-5.96), B = -7.7 (-7.95) (in units of $10^{-5}/T^2$), $\varphi_0 = 18.2^\circ$ (16.6°) (calculated values are given in parentheses). Measurements for three different orientations of the field H_0 show that the magnetostriction in LiTmF₄ changes sign when the field rotates around the *c*-axis. The strong anisotropy of magnetostriction in the basis plane of TmPO₄ crystals was also found by Bondar' et al. (1988): the value of $(\Delta L/L)_{\parallel}$ at T = 4.5 K and $H_0 = 40$ kOe changes by two orders of magnitude, from -4.5×10^{-3} at [110] orientation $(B_{2g}$ -deformation) to about 10^{-5} at [100] $(B_{1g}$ -deformation).

Perturbation theory is no longer applicable when the field-induced deformations reach giant values ~ 10^{-3} (see fig. 10). In strong fields ($H_0 > 15$ kOe) one must take into account the effect of deformation in the energy spectrum of Tm³⁺ ions, i.e., one should use solutions of self-consistent field equations for the electronic order parameters $\langle O_p^q \rangle$; in this case the dependence of magnetostriction on H_0^2 becomes nonlinear, which was observed experimentally by Al'tshuler et al. (1980) and Bondar' et al. (1988).

The giant magnetostriction of LiTmF₄ and TmPO₄ crystals is followed by an essential internal deformation. The sublattice displacements (eq. 97), apart from terms linear in macrodeformation parameters, contain supplementary terms Δw , due to internal stresses induced by a magnetic field. Both terms in eq. (97) are of the same order of magnitude, but they may differ in sign. In principle, direct X-ray measurements of internal deformations are possible, since, e.g., theoretical estimates show that displacements of fluorine sublattices in the LiTmF₄ crystal may reach 6×10^{-4} Å for $H_0 \approx 30$ kOe.

Optical spectroscopy makes it possible to obtain some information on internal deformations induced by a magnetic field at low temperatures in paramagnets containing VV ions in axially symmetric crystal fields. The procedure involves measurements of splittings of the excited non-Kramers doublets in a magnetic field perpendicular to the c-axis. In this case the splitting is linear in the macroscopic and internal strains. The

contribution of the former can be found with the use of piezospectroscopic measurements and the results of direct measurements of the magnetostriction. Thus, estimates may be obtained of the effect of sublattice displacements Δw on the spectral parameters of a VV ion. Recently such complex experiments were carried out on LiTmF₄ crystals by Abdulsabirov et al. (1995). They measured, for example, the maximal 2 cm⁻¹ splitting of the doublet from the ³F₂ multiplet of the Tm³⁺ ion (cf. fig. 22) at helium temperatures in a field of 40 kOe in the basis plane of the lattice, which was much greater than the 0.1 cm⁻¹ splitting of this doublet in the same experimental conditions but in the diluted LiY_{0.99}Tm_{0.01}F₄ crystal due to the second-order effect in the Zeeman interaction only.

The changes in VV ion susceptibility χ_0 , induced by an applied field, define the dependence of elastic constants and sound velocity on the field. Aukhadeev et al. (1981) have measured the relative changes of the echo-signal passage times $(\Delta t/t = \Delta l/l - \Delta v_a/v_a)$ for ultrasound ($v \approx 13-14$ MHz) of different polarizations in cylindrical LiTmF₄ samples at T = 4.2 K, propagating along the applied magnetic field, at different values of the field strength. Relative velocity changes ($\Delta v/v$), modified with regard to longitudinal magnetostriction ($\Delta L/L$)_{||}, are proportional to H_0^2 , have a negative sign and do not exceed 5×10^{-3} by modulus at a field intensity of 20 kOe. The field-induced corrections to elastic constants calculated with perturbation theory agree with the experimental data both by order of magnitude and by sign. In particular, the square of velocity of a quasitransverse elastic wave along the [100] direction [with the polarization in the (001)-plane] equals

$$v_{\rm a}^2 = \frac{1}{2d} \left[(C_{11} + C_{66}) - \sqrt{(C_{11} - C_{66})^2 + 4C_{16}^2} \right]$$

The calculated contributions to the elastic constants in the field $H_0 \parallel [100]$ are $\Delta C_{11} = -0.26$, $\Delta C_{16} = -0.03$, $\Delta C_{66} = -0.04$, in units of $\text{GPa}(H_0/\text{T})^2$ and, respectively, $\Delta v_a(H_0)/v_a = -1.6 \times 10^{-3} (H_0/\text{T})^2$; the measured values can be described as

$$\Delta v_{a}(H_{0})/v_{a} = -1.2 \times 10^{-3} (H_{0}/T)^{2}$$

An analogous weak softening of the elastic constants $C(B_{1g})$ and $C(B_{2g})$ for the VV paramagnet HoVO₄ was observed by Goto et al. (1986) at 1.7 K in a magnetic field $H_0 \parallel [001]$ up to 100 kOe. At higher fields they found a new interesting effect due to the level crossing of the ground singlet and the lower Zeeman sublevel of the nearest excited doublet. In the cross-point ($H_{0c} = 106$ kOe) the elastic constants $C(B_{1g})$ and $C(B_{2g})$ are minimal; if the field intensity is further increased, these constants increase rapidly (to 5–11% at minimum depth of 2–5%) and then become saturated at $H_0 > 130$ kOe. Such behaviour is due to the fast population redistribution of the crossing states of the holmium ion, which have different effective coupling constants with the B_{1g} -, B_{2g} -deformations. Figure 11 compares the above experimental data with the results of calculations by Pekurovskii (1986), obtained with coupling parameters calculated within the framework of an exchange charge model (table 9). The difference between the theoretical and experimental curves is partly due to a disregard of contributions of magnetic dipole–



Fig. 11. The lower part of the Ho³⁺ ion energy spectrum and the elastic constant $C(B_{1g})=2(C_{11}-C_{12})$ of HoVO₄ at 1.7 K in the magnetic field $H_0||c$ (*, the data points are from measurements by Goto et al. (1986); the solid curves are obtained with the crystal field and the electron-deformation coupling parameters from tables 7 and 9).

dipole interactions (eq. 105), which can become comparable to contributions of the singleparticle magnetoelastic coupling mechanism.

Goto et al. (1986) also found that the electron-rotation interaction in VV paramagnets results in rather easily detectable effects, in particular, in the "splitting" of elastic constants as in conventional paramagnets. The velocities of transverse acoustic vibrations in a tetragonal lattice, propagating along the *c*-axis (v_{a1}) and in the basis plane (say, along the *a*-axis) with a polarization vector along the *c* (v_{a2}) , are the same $(v_{a1}^2 = v_{a2}^2 = C_{44}/d)$ in the absence of an applied magnetic field. The measured difference between these velocities in the HoVO₄ crystal at T = 1.7 K, $H_0 \parallel [001]$ increases as H_0^2 , and the difference $\delta C_{44} = C_{xzxz} - C_{xxzx}$ (eq. 104) approaches 2.4×10^{-2} GPa in a field of 80 kOe. When the first term is neglected, the following expression is derived from eq. (96) [corresponding contributions are partly compensated for by the nonlinear electrondeformation interaction, whose parameters are estimated with considerable error (Chan 1985)]:

$$\delta C_{44} = \frac{n}{2\nu} g_J \mu_B H_0 \chi_{x0} : B_{xz}^{(r)}(E_g), \tag{147}$$

where $B_{xx}^{(r)}(E_g)$ are coupling constants with the e_{xx} -deformation. In the absence of the field H_0 the susceptibility χ_{x0} equals zero; when estimating it using perturbation theory in accordance with eq. (86), one obtains for helium temperatures:

$$\delta C_{44} = \frac{n}{\nu} \sum_{k\lambda} \left[\frac{g_{I} \mu_{B} H_{0}}{\varepsilon(\Gamma_{5}^{k})} \right]^{2} \langle \Gamma_{1} | J_{x} | k\lambda \rangle \langle k\lambda | J_{z} | k\lambda \rangle \langle k\lambda | O | \Gamma_{1} \rangle : \boldsymbol{B}_{xz}^{(r)}(E_{g}), \quad (148)$$

where $|k\lambda\rangle$ and $\varepsilon(\Gamma_5^k)$ are the wave functions and energies of the doublet states Γ_5^k in the Ho³⁺ spectrum, and $|\Gamma_1\rangle$ is the wave function of the ground state. Inserting the

parameter values $B_{2,xz}^{(r)1} = -6050$, $B_{4,xz}^{(r)1} = -10700$, $B_{6,xz}^{(r)1} = -3690$, $B_{4,xz}^{(r)3} = -1950$, $B_{6,xz}^{(r)3} = 270$ and $B_{6,xz}^{(r)5} = -4050$ (in units of cm⁻¹), as calculated with the exchange charge model, we obtain $\delta C_{44} = 3.4 \times 10^{-6}$ GPa $(H_0/T)^2$, which practically coincides with the measured one.

The VV magnetization in weak fields, considered in the previous subsection, is linear in H_0 ; the magnetization becomes saturated when the field is increased, since for a J-manifold the limiting value of the electronic moment equals $(-g_1\mu_B J)$. The character of the asymptotic approach of a magnetic moment to the limiting value depends on the specific structure of the ion spectrum in a crystal field, on the intensity of electron-deformation interaction, and on the degree of electronic multipole correlation. The magnetization is an odd function of the applied field, so the initial part of the nonlinear $M(H_0)$ dependence is described by the third-order susceptibility $\chi^{(3)}$: $M = \chi^{(T)}H_0 + \chi^{(3)}H_0^3 + \cdots$. The single-ion contribution to $\chi^{(3)}$, as a rule, results in a decrease of $M_{H}^{(1)}$; its magnitude may be found when considering the fourth-order (in \mathcal{H}_{Z}) corrections to the lanthanide ion energy sublevels. The change of the ion spectrum in the field of self-consistent electronic multipoles and the interaction with deformations e and internal displacements w, induced by a magnetic field, give additional contributions to $\chi^{(3)}$ in lanthanide crystals (Morin et al. 1980, Morin and Schmitt 1990). The free energy of a crystal is a negatively defined quadratic form of the deformation tensor components proportional to H_0^2 , sublattice displacements and mean values of ionic quadrupolar moments. Therefore the corresponding contributions to $\chi^{(3)}$ enlarge $M_{H}^{(1)}$. Thus, the strong electron-deformation interaction in VV paramagnets may be responsible for the anomalous nonlinear behaviour of magnetization at increasing applied magnetic field, when the difference $(\partial M/\partial H_0) - \chi^{(T)}$ is at first proportional to H_0^2 and positive, and then becomes a negative quantity.

loffe et al. (1981) observed such a behaviour of magnetization for a TmPO₄ crystal, taking measurements at temperatures from 1.7 to 40 K in magnetic fields up to 180 kOe. The magnetic moment of samples increases linearly with the field intensity up to 15 kOe for the fields $H_0 \parallel [001]$ and $H_0 \perp [001]$. The magnitudes of susceptibilities $\chi_{\parallel}^{(T)}$ and $\chi_{\perp}^{(T)}$ and their temperature dependence are correctly described by eq. (86) with the energy levels and wave functions of Tm³⁺ ions, calculated with the crystal field parameters of table 7a. When the field intensity is increased, the anisotropy of the magnetic moment in the basal plane of the crystal is manifested clearly.

The single-ionic terms of the nonlinear transverse susceptibility satisfactorily describe only the slowly saturable magnetic moment in [100] direction. The magnetization in the [110] direction increases rapidly in the field intensity range 20–50 kOe, and in higher fields it slowly approaches the maximum value of about $6\mu_{\rm B}$ per ion (fig. 12). On the basis of measurement analysis Andronenko et al. (1983) predicted the giant magnetostriction of the B_{2g} -symmetry in the VV paramagnet TmPO₄; with reasonable estimates of electron– deformation interaction parameters, they correctly interpreted the initial nonlinear part of the function $M_{[110]}(H_0)$ within the framework of perturbation theory. With the piezospectroscopic measurement results (table 9) and the magnetostriction data for the TmPO₄ crystal as obtained by Bondar' et al. (1988), one may calculate the mean



Fig. 12. Measured (Ioffe et al. 1981) and calculated (solid curves, see text) magnetization per Tm³⁺ ion in a TmPO₄ crystal at liquid helium temperature in external fields (1) $H_0 \parallel [110]$ and (2) $H_0 \parallel [100]$.

value of the magnetic moments of the Tm³⁺ ions on the eigenfunctions of the operator $\mathcal{H}_0 + \mathcal{H}_Z + \sum_{pq} B_p^{(r)q}(B_{2g}) O_p^q e(B_{2g})$. Then it appears possible to plot the $M_{[110]}(H_0)$ dependence, actually coinciding with the experimental one without attracting any fitting parameters (curve 1 in fig. 12). The coefficient α in eq. (146), determining the forced magnetostriction, has a maximum absolute value $6 \times 10^{-2} \text{ kOe}^{-2}$ at T = 13 - 14 K in the field $H_0 \parallel [110]$ (Bondar' et al. 1988). With increasing temperature, the anisotropy of the magnetization in the (001) plane diminishes due to redistribution of the populations of the ground singlet and the nearest excited doublet, despite the increase in magnetostriction. Under the combined action of the magnetic field and the strain, the Tm³⁺ ions in the doublet state have a magnetic moment comparable by magnitude to that in the ground state, but with the reversed sign.

In a series of papers by Harley and Manning (1978), Kaplan and Vekhter (1983), Ioffe et al. (1983), Vekhter and Kaplan (1984), and Bondar' et al. (1988), the data on the magnetization and magnetoelastic characteristics of the TmPO₄ crystal were interpreted within the framework of pseudospin formalism, by taking into account only the group of Tm^{3+} ion lower levels in a crystal field (singlet-doublet-singlet). In a self-consistent field approximation, the single-ion Hamiltonian (79) may be written in the form

$$\mathcal{H}_{\mathrm{R, eff}} = \Delta \sigma_0 + \frac{g_\perp}{2\sqrt{2}} \mu_{\mathrm{B}}(H_{0x}\sigma_x + H_{0y}\sigma_y) + \left[B^{(r)}e(B_{2g}) + B'w(B_{2g}) - \lambda \left\langle \sigma_z \right\rangle \right] \sigma_z,$$
(149)

where the operators σ_{α} result from matrices

and the parameters Δ , g_{\perp} , λ , $B^{(r)}$ and B' define the projections of the operators \mathcal{H}_0 , \mathcal{H}_Z , $-\langle \boldsymbol{O} \rangle \boldsymbol{\eta} \boldsymbol{O}$ and $\mathcal{H}_{e-l}^{(1)}$ on the four lowest states of Tm³⁺, with an error which does not exceed 10%.

The temperature dependence of the elastic constant $C_{66}(T)$, the temperature and field dependence of magnetization $M \approx \langle \sigma_x + \sigma_y \rangle$ and of induced magnetostriction $e(B_{2g},H_0) \approx \langle \sigma_z \rangle \approx H_{0x}H_{0y}$ in the field $H_0 \parallel [110]$ are satisfactorily described by operator (149) if the parameters $A = [B^{(r)2}/4vC_{66}(0)] + \mu$, $\mu = [B^{\prime 2}/m_0\omega(B_{2g})^2] + \lambda$ are chosen in an appropriate manner ($\omega(B_{2g}) \approx 330 \,\mathrm{cm}^{-1}$ is the frequency of the B_{2g} -mode in the Brillouin zone center; m_0 is the mass of an oxygen atom). The numerical values of parameters $\Delta \approx 30-38 \text{ cm}^{-1}$, $g_{\perp} \approx 10$, $A \approx 18-25 \text{ cm}^{-1}$, $\mu \approx -(5-10) \text{ cm}^{-1}$, are consistent with the results of their estimates, using the real Tm^{3+} spectrum and the measured constants of the electron-deformation interaction. The advantage of the pseudospin formalism is that it gives a comparatively simple qualitative description of the behaviour of the system in an applied magnetic field. However, some errors are inserted beforehand, due to the difference between the operator (149) and the real projection of $\mathcal{H}_{R, eff}$ (eq. 79) on the space of the studied states, and also to the disregard of a supplementary dependence of model parameters on a magnetic field, which mixes lower and upper groups of states. The strain of B_{2g} symmetry is not induced by the field $H_0 \parallel [100]$, but in this case the susceptibility $\chi_0(B_{2g})$ may be changed essentially due to mixing of the ground state with the excited doublet. In particular, when the magnetic field in the [100] direction increases from 0 to 50 kOe, the strain susceptibility $\chi(\sigma_z, \sigma_z)$ increases by 30%. This increase of $\chi_0(B_{2g})$ in the field $H_0 \parallel [100]$ causes a considerable decrease of the elastic constant C_{66} and leads to a structural phase transition stimulated by the magnetic field (when the condition $C_{66}(H_0) = 0$ is fulfilled); this was first observed by Vekhter et al. (1991). The temperature redistribution of the Tm³⁺ ions among the states with essentially different strain susceptibilities determines the anomalous temperature dependence of the ΔE -effect (the relative change of Young's modulus $[E(H_0) - E(0)]/E(0)$ in the magnetic field) in the TmPO₄ crystal, measured by Kazei and Kolmakova (1993). At low temperatures the ΔE -effect is negative $(\Delta E/E = -0.07 \text{ in a field } H_0 = 40 \text{ kOe at } 4.2 \text{ K})$; with increasing temperature it decreases and changes sign. At temperatures above 25 K ΔE is positive regardless of external field intensity.

The NMR of the VV ions appears to be a very sensitive method to measure the nonlinear transverse susceptibility in crystals with an axial symmetry. For example, ¹⁶⁹Tm NMR studies of the LiTmF₄ crystal at 4.2 K in relatively low magnetic fields (<7kOe) have given $\chi^{(3)}/\chi^{(0)} \approx 3 \times 10^{-10}$ (Al'tshuler et al. 1982).

It should be noted that the parameter λ , responsible for the interaction of lanthanide ions via the phonon field, is always negative, and the corresponding renormalization (eqs. 100 and 101) decreases the efficiency of the electronic subsystem interaction with the lattice. Correlations of the local (Jahn–Teller) deformations essentially affect the response of the lanthanide ions to an applied magnetic field only in the case of sufficiently strong interactions of those ions with macroscopic deformations.

3.3. NMR and local magnetic fields in crystals

3.3.1. Distinctive features of NMR of the host lanthanide ions

We proceed to a more detailed examination of the distinctive features of NMR in Van Vleck paramagnets. Parameters of effective spin Hamiltonians of VV ion nuclei for a number of specific compounds are listed in table 13. First of all, the sharp anisotropy of the paramagnetic shift (as well as susceptibility) tensor in a uniaxial crystal is striking. Thus, the measured main values of tensor α for ¹⁶⁹Tm in TmES at helium temperatures are equal to $\alpha_{\parallel} = 0.364(2)$, $\alpha_{\perp} = 73.2(3)$. The cause of this strong anisotropy in the susceptibility is obvious (see eq. 130 and table 5): the longitudinal field (operator J_z) mixes into the ground state $|g\rangle(\varepsilon=0;\Gamma_1)$ only the high-lying state $|s\rangle(\varepsilon=214.8 \text{ cm}^{-1};\Gamma_2)$, while the transverse field couples $|g\rangle$ with the lowest excited doublet $|d_{1,2}\rangle(\varepsilon=32.1 \text{ cm}^{-1};\Gamma_5)$.

The value of the parameter α_{\perp} [=(γ_{\perp}/γ_I)-1], given in table 13, is slightly different from that given above, since the local magnetic field affecting the ion within a crystal notably differs from an applied field because of the significant value of the VV magnetization in the perpendicular orientation. Calculations for spherical samples show that the ratio

$$\frac{(\gamma_{\perp})_{\text{meas}}}{(\gamma_{\perp})_{\text{true}}} = 1 + \Lambda_{\perp} \chi_{\perp}^{(0)}$$
(150)

equals 1.0028 in TmES and 1.006 in LiTmF₄. Molecular field constants Λ_i are defined by eqs. (76) and (72) and the susceptibility is related to unit volume.

Comparison of the γ -factors obtained experimentally and calculated by means of formulae (130) and (134) makes it possible to verify and determine more exactly the data on a crystal field in samples. Thus, the calculations, using the data of table 5, result in the value $|\gamma_{\parallel}/2\pi| = 0.557$ kHz/Oe, which essentially (~15%) disagrees with the experimental value 0.480 kHz/Oe. A slight modification of the ground-state wave function ($|g\rangle = 0.095(|+6\rangle + |-6\rangle) + 0.991 |0\rangle$ instead of $|g\rangle = 0.119(|+6\rangle + |-6\rangle) + 0.986 |0\rangle$) proves to be sufficient for elimination of the above contradiction.

It should be noted that the transverse component of the VV susceptibility $\chi_{\perp}^{(0)}$ depends on the orientation of the magnetic field in the plane perpendicular to the crystal *c*-axis. This dependence is due to the anisotropy of the electronic Zeeman interaction and to magnetostrictive deformation, as mentioned in sect. 3.2. In the weak fields such an angular dependence was registered only by NMR methods (Al'tshuler et al. 1982).

The strong anisotropy of the thulium NMR paramagnetic shift produces some interesting effects which are not characteristic of normal NMR. The investigation of the angular dependences of the ¹⁶⁹Tm NMR line width and shape in LiTmF₄ has shown that for small angles θ between the direction of an external magnetic field and the crystallographic *c*-axis a solitary NMR line transforms into a spectrum consisting of two or three lines (Korableva et al. 1983). The origin of this "multiplet structure" can be

						Г	able 13						
NMR	parameters	of	lanthanide	ions in	ı the	singlet	ground-state	systems	at	liquid	helium	temperatures.	The
			gyromagn	ietic rat	ios a	re taken	from Abraga	im and B	llea	ney (1	983)		

Isotope	Ι	γ ₁ /2π	$\frac{1}{2\pi}$ Crystal Ref. R-site Parameters of the nuclear spin Hamiltonian							
		$\left(\frac{\mathrm{kHz}}{\mathrm{Oe}}\right)$			symm.	α_x^0	α_y^0	$\overline{\alpha_z^0}$	<i>q</i> ⁰ / <i>h</i> (MHz)	η
¹⁴¹ Pr	5/2	1.29	Pr ₂ (SO ₄) ₃ :8H ₂ O	1, 2	C ₁	2.60	1.10	8.57	5.865	0.124
	-		Pr(NO ₃) ₃ :6H ₂ O	3	Cı	4.82	0.69	12.0	6.550	0.235
			PrF ₃	4	Cs	1.57	1.51	6.78	4.31	0.070
			PrAlO ₃	5	D_{2d}	0.547	0.547	6.21	4.20	
			PrVO ₄	6,7	D _{2d}	5.02	5.02	0.907	3.375	
			Cs ₂ NaPrCl ₆	8	tetr.	1.69	1.69	1.47	0.15	
¹⁵⁹ Tb	$\frac{3}{2}$	0.966	Cs₂NaTbCl ₆	8	tetr.	29.0	29.0	30.7	6.6(?)	
¹⁶⁵ Ho	7	0.898	HoVO ₄	9	D _{2d}	169	169	1.2	25.9	
	2		Rb₂NaHoF ₆	10	tetr.	177	177	43.5	9	
			HoF ₃	17	Cs		576.2			
¹⁶⁹ Tm	$\frac{1}{2}$	-0.354	$Tm(C_2H_5SO_4)_39H_2O$	11	C _{3h}	72.6	72.6	0.356		
	1		LiTmF ₄	11	S ₄	66.5	66.5	1.73		
			Tm ₃ Ga ₅ O ₁₂	, 12		13.5	9.60	23.9		
			$Tm_3Al_5O_{12}$	13	D_2	5.07	2.42	93.1		
			TmVO₄	14	D_2	5.8	26	780(?)		
			TmAsO₄	15	\mathbf{D}_2	16.1	9.8	198		
			TmPO₄	16	D_{2d}	77.0	77.0	2.19		
			$Cs_2NaTmCl_6$	8	tetr.	29.2	29.2	28.7		
Referenc	es									
(1) Al'tsh	uler	and Teplov	(1967) (7) Bleane	ey et al. (1978a)		(13) Jones	and Schmi	dt (1969)	
(2) Teplov (3) Konov	v (19 v and	67) Teplov (1	(8) Bleane (9) Bleane	eyetal.(wetal.(1982c) 1978b)		(14) Blean (15) Blean	ey and We	lis (1980) 9835)	
(4) Al'tsh	uler	et al. (197	9) (10) Egore	ov et al.	(1980)		(16) Blean	iey et al. (1	983c)	

(5) Konov and Teplov (1977) (6) Bleaney et al. (1977)

(11) Aminov and Teplov (1985) (12) Jones (1968)

(17) Bleaney et al. (1988c)

explained by the mosaicity of a single crystal. For a given frequency v of a spectrometer, thulium NMR is observed in the field

$$H = \frac{2\pi\nu}{\gamma_I} \left[(1 + \alpha_{\parallel})^2 \cos^2 \theta + (1 + \alpha_{\perp})^2 \sin^2 \theta \right]^{-1/2}.$$
 (151)

If a crystal consists of several grains with different axes c, each of these grains gives its own NMR line in the field H_i , corresponding to the proper angle θ_i . With a difference in only 12 angular minutes between c-axis orientations of the two grains, the interval separating the corresponding NMR lines at 10.6 MHz reaches 350 Oe. It has been found possible to observe the crystal mosaicity even if the dispersion of the c-axes of different grains does not exceed three angular minutes. Due to such high resolution, the NMR method proved to be very useful for elaborating a technology of growing highquality single crystals of rare-earth tetrafluorides (Korableva et al. 1983). By means of NMR it has been established, in particular, that samples with the direction of the c-axis close to that of the temperature gradient in the crystallization zone during the process of growth, have the most perfect crystal structure.

Abdulsabirov et al. (1979) have investigated NMR in TmES and LiTmF₄ crystals under high hydrostatic pressure. In TmES the γ -factor monotonously decreases with the rise of pressure, which is qualitatively explained by an increase of the crystal potential and the energy intervals between the ground and excited states. However, in LiTmF₄ a sharp increase of the gyromagnetic ratio in the low pressure region, accompanied by an increase of the line width from 13.5 Oe at $P \ge 0.2$ kbar, has been observed.

The considerable difference between ¹⁶⁹Tm NMR parameters in similar crystals TmVO₄ (Bleaney and Wells 1980), TmAsO₄ (Bleaney et al. 1983b), and TmPO₄ (Bleaney et al. 1983c) is accounted for by the different structures of the electronic energy levels of the Tm³⁺ ion (see table 5). An electronic doublet is a ground state of thulium ions in TmVO₄ and TmAsO₄ compounds, and at low temperatures (several degrees Kelvin) they undergo a structural phase transition. As a result of symmetry lowering, the doublet splits into two singlets, and this permits the observation of ¹⁶⁹Tm NMR.

The results of the investigation of thulium hexachloride (Bleaney et al. 1982c), as well as of praseodymium and terbium hexachlorides, may be interpreted by assuming that the R^{3+} ion is placed in a field of cubic symmetry with a small tetragonal distortion. The singlet Γ_1 is the ground state of the Tm^{3+} ion, and the nearest excited state (with the excitation energy 58 cm⁻¹) represents a Γ_4 triplet slightly split by tetragonal perturbation. As a result the γ -factor proves to be only slightly anisotropic.

In Cs₂NaTbCl₆ Bleaney et al. (1982c) have found a deviation from cubic to tetragonal symmetry in the Tb³⁺ position, the deviation occurring gradually only at temperatures below 20 K and becoming constant at temperatures below 10 K. The data obtained make it possible to estimate an energy of a Γ_4 triplet relative to a Γ_1 singlet as 36 cm^{-1} , and the magnitude of tetragonal splitting of Γ_4 as 1.6 cm^{-1} , the tetragonal singlet being the lower sublevel. The calculated value of the quadrupolar interaction constant is q/h=-6.6 MHz. However, only one line is observed in the experiment, corresponding apparently to the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition, while two other lines prove to be too weak because of deformational inhomogeneous broadening.

NMR spectra of ¹⁵⁹Tb in Rb_2NaTbF_6 also suggest that the crystal field symmetry in the terbium ion site differs from cubic at liquid helium temperatures (Tagirov et al. 1979).

Now we turn to the NMR spectra of ¹⁴¹Pr $(I = \frac{5}{2})$. The NMR of lanthanide ions with the singlet ground state has been first observed in experiments with hydrated praseodymium sulfate Pr₂(SO₄)₃·8H₂O (Al'tshuler and Teplov 1967, Teplov 1967), whose magnetic properties were also studied by Penney and Schlapp (1932). The crystal belongs to a monoclinic system, its space group is C2/c (C⁶_{2h}), and the unit cell contains four molecules. The praseodymium atoms occupy general positions in a crystal, so there are two magnetically conjugated NMR spectra. In interpreting the spectra the principal axes of the γ tensor were assumed to coincide with those of the quadrupolar interaction tensor.

Local axes x, y, z (chosen in such a way that $\alpha_y < \alpha_x < \alpha_z$) between identical axes for two types of Pr^{3+} centers were found to be

$$\widehat{x_1x_2} = 56(3)^\circ, \qquad \widehat{y_1y_2} = 76(2)^\circ, \qquad \widehat{z_1z_2} = 97(5)^\circ.$$

In PrF_3 there are three types of magnetically equivalent Pr^{3+} centers, all being described by one spin Hamiltonian of rhombic symmetry (Al'tshuler et al. 1979).

Praseodymium aluminate, PrAlO₃, is well known because of the instability of its crystal structure, and it has been the object of numerous investigations by EPR (Harley et al. 1973, Cohen et al. 1974, D'Iorio et al. 1984), optical (Riseberg et al. 1969, Cohen et al. 1969, Harley et al. 1975, Lyons et al. 1975, Glynn et al. 1975), and neutron (Birgeneau et al. 1974) spectroscopy methods. It has been found that $PrAlO_3$ has the cubic perovskite structure only at temperatures higher than 1320 K, and at lower temperatures it undergoes several structural phase transitions: cubic to rhombohedral (1320 K), rhombohedral to orthorhombic (205 K), orthorhombic to monoclynic (151 K), and further at T < 77 K to tetragonal (transitions of the second, first, and second orders, respectively). It has also been found (Birgeneau et al. 1974) that transitions at 205 and 151 K occur as a result of the competition between the electronic and the elastic contributions to the total energy of a crystal. The distortions of the PrAIO₃ crystal lattice at different phase transitions are due to rotations of AlO_6 octahedra around some axis. The direction of this axis changes when the temperature is lowered while the rotation angles remain approximately constant $(\pm 9.4^{\circ})$. At temperatures between 205 and 1320K the rotation axis coincides with the [111] direction of the perovskite lattice, in the temperature range 151–205 K the axis is oriented along [101], and at temperatures below 151 K this axis moves continuously in the direction from [101] to [001], so that the crystal symmetry becomes tetragonal at T < 77 K. However, according to the data of D'Iorio et al. (1984) no precise tetragonal symmetry is achieved even at liquid helium temperatures. Perhaps this is due to the substantial amount of Gd³⁺ impurity in the samples studied.

At low temperatures the crystal space group is I4/mcm (D_{4h}^{18}), the point group symmetry of Pr^{3+} surroundings is D_{2d} , local axes of the second order are oriented along [110] and [110] and the fourth order axis is along [001]. Since usually all three cubic axes of the perovskite structure are equivalent, a PrAlO₃ crystal consists of three kinds of tetragonal domains oriented along [100], [010], and [001]. However, in the presence of a strong magnetic field (~20 kOe) or a small uniaxial pressure (~0.5 bar) the sample can turn into a single-domain state (Riseberg et al. 1969).

The multidomain structure of PrAlO₃ was observed in the very first measurements of the ¹⁴¹Pr NMR at liquid helium temperatures (Konov and Teplov 1977). When a sample is placed within a cryostat in such a manner that a radiofrequency field H_1 is oriented along a tetragonal axis, a spectrum related to domains oriented along H_1 is observed (here $\gamma^0_{\perp} < \gamma^0_{\parallel}$, see table 13). The spectral lines are characterized by large width and low intensity.

The pattern of the Pr^{3+} (4f², ${}^{3}H_{4}$) ion energy level splitting was established by means of optical (Harley et al. 1973, Lyons et al. 1975) and neutron (Birgeneau et al. 1974)

Energy (cm ⁻¹)	Wave function	Energy (cm ⁻¹)	Wave function
0	$0.598(4\rangle + -4\rangle) - 0.533 0\rangle$	319	$0.887 \pm3 angle+0.462 \mp1 angle$
35	$(2\rangle - -2\rangle)/\sqrt{2}$	445	$0.462 \pm3 angle$ - $0.887 \mp1 angle$
117	$(4\rangle - -4\rangle)/\sqrt{2}$	925	0.377(4 angle+ -4 angle)+0.846 0 angle
224	$(2\rangle + -2\rangle)/\sqrt{2}$		

spectroscopies. With numerical values of the paramagnetic shift as a result of NMR experiments, unknown coefficients of stationary state wave functions can be determined. The best agreement with the experiment is achieved with the following data

These data result in the value of $\gamma_{\perp}^0/2\pi = 2.114 \text{ kHz/Oe}$, which exceeds the measured one by 6%. Possibly, this is due to the influence of the excited multiplet level ${}^3\text{H}_5$ separated from the ground multiplet by a fairly small interval of 2100 cm^{-1} .

Analogous calculations of the Pr^{3+} ion wave functions in $PrVO_4$ were carried out by Bleaney et al. (1978a). The situation in praseodymium vanadate is a rather interesting one, since the lowest excited level proves to be a singlet (excitation energy 35 cm^{-1} at low temperatures), which is not coupled with the ground level by matrix elements of the momentum J. The Van Vleck susceptibility of the excited singlet in the direction of the *c*-axis exceeds by far the susceptibility of the ground singlet. This causes a sharp increase of γ_{\parallel} with the temperature in the range of 8–20 K.

NMR spectra of ¹⁶⁵Ho have been studied in detail in the following VV paramagnets: HoVO₄ (Bleaney et al. 1978b), elpasolites Rb₂NaHoF₆ (Egorov et al. 1980, Tagirov et al. 1979), Cs₂NaHoF₆ (Veenendaal and Brom 1982, Veenendaal et al. 1983), and Cs₂NaHoCl₆ (Bleaney et al. 1981b), in holmium trifluoride HoF₃ (Bleaney et al. 1988b), and in holmium nicotinate $H_0(C_5H_4NCO_2)_32H_2O$ (Bleaney et al. 1990). The first of the systems mentioned has a distinct tetragonal symmetry, and the anisotropy of an effective nuclear gyromagnetic ratio in this case is the highest of those reported in literature (see table 13). The closest to the ground level electronic doublet has a relative energy of 21 cm⁻¹, therefore $|\gamma_{\perp}^0/2\pi|$ reaches a very large value of 152.6 kHz/Oe and remains constant (within 0.2-0.3%) in the plane perpendicular to the tetragonal axis. This experimental fact definitely confirms an axial symmetry and testifies that the doublet splitting observed in optical experiments (Battison et al. 1975) is not related to static crystal distortion. (This effect has been explained as the Davydov splitting due to magnetic interactions between Ho³⁺ ions (Aminov 1981).) Precise determination of γ_{\parallel} has been complicated because of the high anisotropy. Experiments have been carried out both with concentrated HoVO₄ and with magnetically diluted YVO₄ containing 2% Ho ions.

In experiments on the Cs₂NaHoCl₆ system in the temperature range 0.6–20 K no deviations from cubic symmetry have been found. The system is of special interest since its ground state is not a singlet, but a nonmagnetic doublet Γ_3 with the nearest triplet Γ_4 (excitation energy $\Delta_4 = 10.3$ cm⁻¹) and the singlet Γ_1 ($\Delta_1 \approx 30$ –40 cm⁻¹). The isotropic γ -

factor reaching a value of 198 kHz/Oe at 2 K, is reduced to 70 kHz/Oe at 20 K. Though in principle a nuclear Hamiltonian contains a quadrupolar term, only one NMR line has been observed in the experiment, since the linewidth exceeds possible values of quadrupolar splitting (Abragam and Bleaney 1982).

The solitary ¹⁶⁵Ho NMR line has also been observed by Veenendaal and Brom (1982) in a Cs₂NaHoF₆ single crystal at temperatures above 2 K. According to heat capacity measurements in the zero field (Veenendaal et al. 1983) the degeneracy of the ground doublet Γ_3 in this compound is lifted at T_D =393 mK; the corresponding phase transition is described as the cooperative Jahn–Teller effect. At 20 mK the effective gyromagnetic ratio along the [001] axis appreciably exceeds that ratio of 4.2 K and reaches the value of 233 kHz/Oe.

Another picture is observed in Rb₂NaHoF₆ (Egorov et al. 1980). The appearance of two comparatively narrow spectra instead of a broad one shows that they are due to tetragonal ¹⁶⁵Ho³⁺ centers. High intensity of spectra leaves no doubt that the resonance absorption is caused by all the holmium ions and not by a small number of defect centers which might be due to imperfections of the crystal structure. Therefore one has to assume that the Rb₂NaHoF₆ crystal, similar to praseodymium aluminate, consists of tetragonal structural domains oriented along elpasolite cubic axes. Apparently, the phase transition temperature in this crystal proves to be much higher than in Cs_2NaHoF_6 . Indeed, an investigation of polycrystalline Rb₂NaHoF₆ samples shows the existence of a phase transition from cubic phase Fm3m to tetragonal I4/m at 172K (Ihringer 1982). Measurement of the heat capacity of the monocrystalline sample gives a typical peak corresponding to the structural phase transition at 169K (Zhdanov et al. 1983). An analysis of the temperature dependence of the spin Hamiltonian parameters in the temperature range 1.6-16 K shows that the magnetic properties of the crystal in a low-temperature phase are determined by a group of 4f-electron states close in energy and generated from the cubic states Γ_3 (ground doublet), Γ_4 (triplet), and Γ_1 (singlet) by a small tetragonal distortion of the crystal potential.

An enhanced nuclear resonance spectrum of the ¹⁶⁵Ho nucleus was observed by Bleaney et al. (1988b) in a HoF₃ single crystal at 3.52 GHz and 1.6 K. Taking into account corrections due to the difference between applied and internal field (see eq. 150) and the saturation effects, they obtained a very large value, $a \approx 665$, for the shift tensor in the direction of the crystallographic *a*-axis. The separation between the two lowest singlet states was found to be 6.59 cm^{-1} .

A great enhancement was observed by Bleaney et al. (1990) for ¹⁶⁵Ho NMR spectrum in holmium nicotinate. The optical absorption spectrum of this compound shows that the lowest level of the Ho³⁺ ion is a singlet, with two other singlets at 8.1 and 15 cm⁻¹. At 4.2 K the value of the paramagnetic shift α varies from 352 to 76 in the plane of reflection symmetry.

The NMR parameters in table 13 are given for liquid helium temperatures. As the temperature is raised, excited electronic states are populated, and the nucleus is subjected to the influence of different hyperfine fields, fluctuating due to the random processes of thermal activation and deactivation. Now, in place of a single precession frequency for



Fig. 13. Temperature dependence of the paramagnetic shift of ¹⁶⁹Tm NMR in TmES. The curves present the result of calculations using the relation $a^{T} \propto \chi^{T}$ (Aminov et al. 1983).

the nuclear spin, there appears a spectrum of frequencies. For sufficiently rapid changes in the electronic states a single line is observed as before; however this line undergoes an additional shift if the frequency spectrum under discussion is not symmetric relative to the NMR frequency of the VV ions in the singlet state. A temperature dependence of this kind in the NMR line shift a^T has been observed for the first time by Jones (1967) while investigating intermetallic compounds of praseodymium and thulium. Later this effect was also observed in dielectric compounds of thulium (Aukhadeev et al. 1973, Konov and Teplov 1976b), praseodymium (Bleaney et al. 1977), and holmium (Egorov et al. 1980). The experimental results can be well interpreted by use of the relation $a^T \propto \chi^T$, which is based on the substitution of a time averaged value for the hyperfine field on a statistically averaged value (cf. fig. 13).

The temperature-dependent shift of the resonance line is strongly connected with the nuclear magnetic relaxation times and the linewidth. The fluctuating magnetic field at the nucleus usually has components perpendicular to the external magnetic field. The Fourier spectrum of these field components contains terms with resonance frequencies, which induce transitions between nuclear energy levels. One may foresee the temperature

dependence of relaxation rates T_1^{-1} and T_2^{-1} taking into account that the corresponding correlation functions of electronic magnetization are to contain the probabilities of transitions to excited states, i.e. Boltzmann factors $\exp(\Delta/k_B T)$. The nuclear relaxation will be considered in more detail in the following subsection.

3.3.2. NMR of diamagnetic ligands

The presence of VV ions in crystals must be appreciably reflected in the NMR spectra of diamagnetic atoms of the matrices. If a ligand is separated from a paramagnetic ion by a large distance (≥ 3 Å), their multipolar interaction is mainly the magnetic dipole-dipole one. Calculations by Eremin et al. (1977) show that even in the LiTmF₄ crystal, which is notable for its comparatively dense packing, the contributions of higher moments (neglecting overlap effects) are much less than the dipolar ones. In such cases the shift, splitting, and broadening of resonance lines can be analyzed in a precise quantitative manner, and we may assume the NMR spectra of ligands to contribute to a determination of exact coordinates of atoms in a crystal lattice. In crystals with dense atomic packing a manifestation of overlap of lanthanide ions and electronic orbits of ligands is to be expected. Thus, a study of the NMR spectra of ligands must disclose the role of the electron exchange in ligand hyperfine interaction and yield values of isotropic and anisotropic contributions and their temperature dependences.

The effective nuclear spin Hamiltonian of a ligand v has a form analogous to eqs. (135) and (136):

$$\mathcal{H}_{\mathbf{v}} = -\gamma_{I} \hbar \boldsymbol{H}_{0}(1+\lambda_{\mathbf{v}}) \boldsymbol{I}_{\mathbf{v}} + q_{\boldsymbol{v}\alpha\beta} \left(\boldsymbol{I}_{\boldsymbol{v}\alpha} \boldsymbol{I}_{\boldsymbol{v}\beta} - \frac{1}{3} \delta_{\alpha\beta} \boldsymbol{I}_{\boldsymbol{v}}^{2} \right), \tag{152}$$

where the shift tensor λ_{v} includes dipolar fields of induced moments of VV ions, and the corresponding contribution is obtained by the calculation of lattice sums

$$\lambda_{\nu\alpha\beta}^{(d)} = \frac{\nu}{n} \chi_{\alpha\gamma}^{(T)} \sum \left(r^2 \delta_{\gamma\beta} - 3x_{\gamma} x_{\beta} \right) r^{-5}.$$
(153)

"Pseudoquadrupolar" terms, quadratic in dipole-dipole interaction, are very small and therefore negligible. To avoid the complications connected with the demagnetization field factors, it is convenient to consider the spherical samples. In this case the sum in eq. (153) is taken over the sphere of a sufficiently large radius centered on a ligand ion.

The Zeeman part of the Hamiltonian (152) is readily diagonalized, and the effective field is determined by equation

$$H = H_0 [(1 + \lambda_\nu)_{\alpha\beta} (1 + \lambda_\nu)_{\alpha\gamma} l_\beta l_\gamma]^{1/2}$$
(154)

where l_{α} are direction cosines of an applied field. The paramagnetic shift in this case is much less than for the nuclei of VV ions, $(|\lambda_v| \ll 1)$, so the following approximate formula is appropriate:

$$H \approx H_0 (1 + \lambda_{\nu \alpha \beta} l_\alpha l_\beta). \tag{155}$$

In TmES, LiTmF₄ and some other uniaxial crystals the $\chi_{\parallel}^{(0)}$ components of the VV susceptibility are very small, and the NMR spectra of ligands in the field $H_0 \parallel c$ are

of no practical interest. Let the magnetic field be perpendicular to the c-axis (z) and at angle ϕ to the *a*-axis (x) ($l_z = 0$, $l_x = \cos \phi$, $l_y = \sin \phi$). Then

$$\frac{H}{H_0} - 1 \approx \frac{v}{n} \chi_{\perp}^{(0)} \left(\frac{\Sigma_1 + \Sigma_2}{2} + \cos 2\phi \frac{\Sigma_1 - \Sigma_2}{2} - \sin 2\phi \Sigma_3 \right),$$
(156)

where

$$\Sigma_1 = \sum (r^2 - 3x^2) r^{-5}, \qquad \Sigma_2 = \sum (r^2 - 3y^2) r^{-5}, \qquad \Sigma_3 = 3 \sum xyr^{-5}, \qquad (157)$$

and the summation is over all lanthanide (VV) ions surrounding the chosen nucleus.

The width of the proton magnetic resonance spectrum in the TmES crystal reaches almost 8% of the applied magnetic field at liquid helium temperatures (Teplov 1968). It is possible to attempt to determine coordinates of hydrogen atoms by studying the dependence of the above spectrum on the angle ϕ (Egorov et al. 1984b). The positions of all atoms in the YES lattice have been determined by the neutron diffraction method (Broach et al. 1979), so only the lattice parameters of the TmES crystal at liquid helium temperature can be regarded as unknown quantities. To find them it is sufficient to determine the coordinates of some protons. Protons of crystallization water (H4, H5A, H5B, see table 1) are closest to a rare-earth ion: they are affected by strong local fields and their lines in NMR spectra in the field $H_0 \perp c$ prove always to be extreme. Therefore



Fig. 14. (a) Relative values of the local magnetic fields at H4, H5A and H5B protons belonging to water molecules and (b) the width of the proton magnetic resonance spectrum, in a TmES crystal at 4.2 K (Egorov et al. 1984b). The external field H_0 is perpendicular to the *c*-axis; ϕ is the angle of H_0 with the *a*-axis; solid lines are the results of calculations with the lattice parameters $a_0 = 13.59$ Å, $c_0 = 6.86$ Å; the dashed line is calculated using the YES lattice parameters.



Fig. 15. Relative values of the local magnetic fields at the ¹⁹F nuclei in the LiTmF₄ crystal, the magnetic field is perpendicular to the *c*-axis; ϕ is the angle of H_0 with the *a*-axis; the solid lines are the results of calculations using the formulae (156) and (157); the open circles are the experimental values: (a) temperature 77 K, frequency 19.5 MHz; (b) temperature 4.2 K, frequency 9.5 MHz.

the problem is reduced to the choice of such lattice parameters that the differences of the calculated resonance fields of protons H5A, H5B, and H4 coincide with the measured values of the width of the NMR spectrum. Local fields on the crystallization water protons have been calculated with lattice parameters $a_0 = 13.59$ Å, $c_0 = 6.86$ Å; the results are given in fig. 14. In calculations the value $\chi_{\perp}^{(0)} = 7.07 \times 10^{-25}$ cm³/ion for the VV susceptibility of the Tm³⁺ ion has been used, which is obtained from the measured paramagnetic shift of ¹⁶⁹Tm NMR by use of the following numerical values of the Landé factor and the hyperfine interaction constant: $g_J = 1.1638$, $A_J/h = -393.5$ MHz (Judd and Lindgren 1961, Abragam and Bleaney 1970). The calculated value of the spectrum width (solid curve in fig. 14b) is in a good agreement with the measured one. For comparison the results of a similar calculation with YES lattice parameters exceeding those mentioned above by only 2% are shown in the figure (dashed curve).

The NMR spectra of ¹⁹F in LiTmF₄ have been studied at frequencies 10–20 MHz in magnetic fields 2.5–5 kOe (Eremin et al. 1977, see fig. 15). F⁻ ions take two nonequivalent positions in the lattice of the LiTmF₄ crystal, so two NMR lines of ¹⁹F are observed in the field $H_0 \perp c$, whose location depends on orientation of H_0 relative to the crystallographic

					Table 14							
NMR	parameters	of diamagnetic	ligands ir	1 some	dielectric	c crystals	of the	Van	Vleck p	aramagnet	s at	: liquid
				heliun	n temper	atures						
											-	

Isotope	Ι	$\gamma_I/2\pi$ (kHz/Oe)	Crystal	Ref.	Magnetic field direction	VV suscept. $\chi^{(0)}_{aa}$ (cm ³ /mol)	Paramagn. shift $\lambda_{\nu,\alpha\alpha} \times 10^3$	Quadrup. parameter q/h (kHz)
'Η	$\frac{1}{2}$	+4.2575	TmES	1	$H_0 \perp c$	0.426	$\lambda_{vmax} = +34 (H5A);$ $\lambda_{vmin} = -41 (H4)$	-
¹⁹ F	$\frac{1}{2}$	+4.0054	LiTmF ₄	2	$H_0 \perp c$	0.392	$\lambda_{v \max} - \lambda_{v \min} = 109$	-
²³ Na	$\frac{3}{2}$	+1.1262	$Cs_2NaHoCl_6$	3	$H_0 \ [111]$	1.68	-6	0
³¹ P	$\frac{1}{2}$	+1.7235	TmPO ₄	4	$H_0 \parallel c;$	0.0129	+2.4	
					$H_0 \perp c$	0.450	-28.9	~
⁵¹ V	$\frac{7}{2}$	+1.1193	PrVO ₄	5,6	$H_0 \parallel c$	0.010	≤+1	189.5
					$H_0 \perp c$	0.032	≥-1	
^{51}V			EuVO ₄	5,6	$H_0 \parallel c$	0.0063	~0	178.9
					$H_0 \perp c$	0.0055	~0	
⁵¹ V			HoVO₄	5,6	$H_0 \parallel c$	0.011	0	165.6
					$H_{\rm 0} \perp c$	1.30	-35	
⁵¹ V			TmVO₄	7	$H_0 \parallel [110]$	0.0933	$\lambda_{v,xx} = -1.9$	158.7
							$\lambda_{v,yy} = -5.0$	156.0

References

(1) Aminov and Teplov (1985)

(4) Bleaney et al. (1983c)(5) Bleaney et al. (1982b)

(2) Eremin et al. (1977)(3) Bleaney et al. (1981b)

a-axis. Both NMR lines have fine structure at low temperatures, due to interaction of the nuclei with the nearest thulium ions. The spectrum width (an interval between centers of two groups of lines) is proportional to an applied magnetic field. The width is maximal if the angle ϕ between the magnetic field and the *a*-axis is equal to 23 $(\pm 90n)^{\circ}$, and the spectrum is reduced to a solitary line at $\phi = 68^{\circ}$ (fig. 15). At 4.2 K and below, the maximum width reaches 0.109 of the resonance field H_0 of the "free" fluorine nuclei and is equal to $0.0273 H_0$ at 77 K. The spectrum center is shifted to fields higher than H_0 . This shift is also proportional to an external field and equals $0.0350 H_0$ at 4.2 K and $0.0066 H_0$ at 77 K. The angular dependence of resonance fields of two nonequivalent fluorine nuclei, calculated using eqs. (156) and (157), is shown by solid lines in fig. 15. The molar susceptibility of the LiTmF₄ crystal has been taken to be equal to $0.392 \text{ cm}^3/\text{mol}$ at 4.2 K as calculated using eq. (130). The calculated dipolar contributions to isotropic and anisotropic components of the ¹⁹F NMR line shift are equal to 15 and 74% of the observed values, respectively. This indicates the additional interaction between the Tm³⁺ ions and ¹⁹F nuclei, which appears, most probably, due to the overlap of thulium 4f-electron orbits with 1s, 2s, and 2p orbits of F⁻ ion (transferred hyperfine interactions).

⁽⁶⁾ Bleaney et al. (1982a)

⁽⁷⁾ Bleaney and Wells (1980)

Nondipolar interactions of nuclei of diamagnetic ligands with VV ions in a number of compounds have been investigated by Bleaney et al. (1978b, 1981b, 1982b, 1983c). The contribution of transferred hyperfine interactions to the paramagnetic shift for ⁵¹V in HoVO₄ and ³¹P in TmPO₄ proves to be quite comparable with a similar contribution in LiTmF₄, in spite of the fact that in those crystals the transfer of spin density can occur only via the intermediate O^{2-} ion.

A clear shift of ²³Na and ¹³³Cs NMR lines, proportional to the effective γ -factor of the Ho³⁺ ion, has been observed in Cs₂NaHoCl₆ by Bleaney et al. (1981b). After subtracting contributions of the Lorentz and demagnetizing fields, there remains a small paramagnetic shift λ_{ν} (≈ 0.006 for Na and even less for Cs), which for Na and Cs atoms, placed in the cubic positions of elpasolite, can occur only due to the transferred hyperfine interaction. ENDOR experiments directly testify to the presence of the above interaction in elpasolites with lanthanide ions (Fish and Stapleton 1978).

Some results of experimental NMR investigations of diamagnetic atoms in Van Vleck paramagnets are summarized in table 14.

3.3.3. Magnetic resonance line shape for nuclei of Van Vleck ions

The essential sources of the NMR line broadening for VV ions are: (a) imperfections of a crystal structure; (b) dipole-dipole interactions of VV ions with each other, with nuclei of diamagnetic ligands, with electronic moments of impurity ions; and (c) unresolved fine structure of the NMR spectra for ions with spin $I > \frac{1}{2}$.

Crystal structure defects involve the local spread of crystal axes directions. They distort the structure of energy levels and the wave functions of VV ions, and by way of these quantities, according to eqs. (130) and (134), they change the paramagnetic shift tensor α and the gyromagnetic ratio $\gamma = \gamma_I (1 + \alpha)$. The corresponding change of the resonance frequency equals $\Delta \omega_0 = H_0 \Delta \gamma$, where γ is the effective γ -factor. Assuming deviations $\Delta \gamma_{\parallel}$, $\Delta \gamma_{\perp}$ and $\Delta \theta$ are independent, the following equation for the second moment of the resonance line in axial crystals is obtained (Egorov et al. 1979):

$$M_{2}^{(\alpha)} = \langle \Delta \omega_{0}^{2} \rangle$$

= $\frac{\omega_{0}^{2}}{\gamma^{4}} \left\{ \left\langle \Delta \gamma_{\parallel}^{2} \right\rangle \gamma_{\parallel}^{2} \cos^{4} \theta + \left\langle \Delta \gamma_{\perp}^{2} \right\rangle \gamma_{\perp}^{2} \sin^{4} \theta + (\gamma_{\perp}^{2} - \gamma_{\parallel}^{2})^{2} \cos^{2} \theta \left\langle \Delta \theta^{2} \right\rangle \right\}.$ (158)

The distinctive feature of this term is its quadratic dependence on the resonance frequency. Studies of the frequency and angular dependences of M_2 have shown that the principal cause of inhomogeneous NMR line broadening in such crystals as TmES and LiTmF₄ is scatter in the values of the perpendicular component of the paramagnetic shift α_{\perp} (Egorov et al. 1984b).

Accounting for spin-spin contributions to the line broadening is complicated by the different gyromagnetic ratio tensors of interacting particles, and the quantization axes of two spins may also be different. Assuming the Z, Z' axes of the local coordinate systems

to be the quantization axes of spins I and S, the secular part of the interaction $\mathcal{H}_{IS} = SPI$ is written as follows:

$$\mathcal{H}_{IS}^{(\text{sec})} = P_{ZZ'} S_{Z'} I_Z + \frac{1}{2} (P_{XX'} + P_{YY'}) (S_{X'} I_X + S_{Y'} I_Y) \,\delta(\omega_S, \omega_I),$$
(159)

the second term being nonzero only for coinciding resonance frequencies. When calculating the second moment with the Hamiltonian (159) it is necessary to keep in mind that an effective alternating field on different spins may differ both in value and direction even if they have the same resonance frequency. We shall come across this case below (sect. 4.5.3) when considering ferromagnetic compounds. In the present case the local coordinate systems of all nuclei of the VV ions coincide. They are plotted for an axial crystal in fig. 16. For VV paramagnets an internal magnetic field H (eq. 154) differs from the applied one H_0 only slightly, and this difference is neglected in line shape calculations. Then the conventional momentum calculation (Al'tshuler and Kozyrev 1972) yields the result

$$\hbar^2 M_2^{(IS)} = \frac{1}{3} I(I+1) \sum \left[P_{ZZ'} - \frac{1}{2} (P_{XX'} + P_{YY'}) \,\delta(\omega_S, \omega_I) \right]^2, \tag{160}$$

where the summation is over all spins S. For dipole-dipole interactions

$$P_{XX'} = \frac{\hbar^2}{r^3} \gamma^{(I)}_{\alpha\beta} \gamma^{(S)}_{\alpha'\beta'} A_{X\beta} A_{X'\beta'} \left(\delta_{\alpha\alpha'} - \frac{3r_{\alpha}r_{\alpha'}}{r^2} \right), \tag{161}$$

where $\gamma^{(I)}, \gamma^{(S)}$ are gyromagnetic ratio tensors for particles *I*, *S*; the Greek indices relate to the crystallographic coordinate system, and $A_{X\alpha}$ is the matrix of transition to the local coordinate system, which in the case of fig. 16 is:

$$\widehat{A} = \begin{pmatrix} \sin\phi & -\cos\phi & 0\\ \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta\\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{pmatrix}.$$
(162)

To calculate the lattice sums it is advisable to use the crystallographic coordinate system, where the tensors $\gamma^{(I)}$ and $\gamma^{(S)}$ are diagonal, and we proceed with the consideration of the interactions mentioned at the beginning of this subsection. For interactions of the VV ions with each other $\gamma^{(I)} = \gamma^{(S)}$, and the corresponding contribution to the second moment of a NMR line appears equal to

$$M_{2}^{(II)} (\operatorname{rad}^{2}/\operatorname{s}^{2}) = \frac{\hbar^{2}}{4\gamma^{4}} \bigg[\frac{1}{16} (2\gamma_{\parallel}^{2} + \gamma_{\perp}^{2})^{2} (2\gamma_{\parallel}^{2} \cos^{2}\theta - \gamma_{\perp}^{2} \sin^{2}\theta)^{2} \Sigma_{6} + \frac{81}{8} \gamma_{\parallel}^{4} \gamma_{\perp}^{4} \sin^{2} 2\theta \Sigma_{7} + \frac{81}{32} \gamma_{\perp}^{8} \sin^{4}\theta (\Sigma_{8} + \cos 4\phi \Sigma_{9}) \bigg],$$
(163)



Fig. 16. Laboratory (x, y, z) and local (x_i, y_i, z_i) coordinate systems.

where

$$\Sigma_{6} = \sum (r^{2} - 3z^{2})^{2} r^{-10}, \qquad \Sigma_{7} = \sum z^{2} (x^{2} - y^{2}) r^{-10},$$

$$\Sigma_{8} = \sum (x^{2} + y^{2})^{2} r^{-10}, \qquad \Sigma_{9} = \sum (x^{4} - 6x^{2}y^{2} + y^{4}) r^{-10}.$$
(164)

It is taken into consideration, that lanthanide ions occupy axial symmetry positions; in

the case of trigonal symmetry (as for TmES) the sum Σ_9 equals zero. For ligand nuclei the gyromagnetic ratio γ_v is isotropic $[\gamma_{\alpha\beta}^{(S)} = \gamma_v \delta_{\alpha\beta}], \omega_S \neq \omega_I$, and the contribution of the VV ion-ligand interaction into the second moment of VV ions NMR line is

$$M_{2}^{(I\nu)} = \frac{1}{3}I_{\nu}(I_{\nu}+1)\left(\frac{\gamma_{\nu}^{2}\hbar^{2}}{\gamma^{2}}\right)\left[\frac{1}{4}(2\gamma_{\parallel}^{2}\cos^{2}\theta - \gamma_{\perp}^{2}\sin^{2}\theta)^{2}\Sigma_{6} + \frac{9}{8}(\gamma_{\parallel}^{2} + \gamma_{\perp}^{2})\sin^{2}2\theta\Sigma_{7} + \frac{9}{8}\gamma_{\perp}^{4}\sin^{4}\theta(\Sigma_{8} + \cos 4\phi\Sigma_{9} + 4\sin 4\phi\Sigma_{10})\right]$$
(165)

where

$$\Sigma_{10} = \sum xy(x^2 - y^2) r^{-10}.$$



Fig. 17. Angular dependence of the second moment of the ¹⁶⁹Tm NMR line in the TmES crystal at 4.2 K and 3.88 MHz; A, crystal lattice defects; B, dipole-dipole interaction of thulium nuclei; C, dipole-dipole interaction of the thulium nuclei with protons; D, dipole-dipole interaction of the thulium nuclei with Tb³⁺ (4.6×10^{-4}) impurity ions; E, the sum of A-D.

For impurity paramagnetic ions one has $\gamma^{(S)}\hbar \rightarrow -g\mu_{\rm B}$, and upon introducing the notation $g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$, where g_{\parallel} and g_{\perp} are the principal values of the *g*-tensor, one obtains

$$M_{2}^{(IS)} = \frac{1}{3}f S(S+1)\frac{\mu_{\rm B}^{2}}{g^{2}\gamma^{2}} \left[\left(\frac{1}{2}g_{\perp}^{2}\gamma_{\perp}^{2}\sin^{2}\theta - g_{\parallel}^{2}\gamma_{\parallel}^{2}\cos^{2}\theta \right)^{2}\Sigma_{6} + \frac{9}{8}(g_{\perp}^{2}\gamma_{\parallel}^{2} + g_{\parallel}^{2}\gamma_{\perp}^{2})^{2}\sin^{2}\theta\Sigma_{7} + \frac{9}{8}g_{\perp}^{4}\gamma_{\perp}^{4}\sin^{4}\theta(\Sigma_{8} + \cos 4\phi\Sigma_{9}) \right].$$
(166)

Here $f = n_S/n_I$ is the relative concentration of impurity paramagnetic centers. When calculating the lattice sums in eq. (166), the contribution of the nearest impurity ions is neglected, since the strong local fields, produced by these ions, bring the resonance frequency of nuclei of the VV ions far outside of the observed line width. For practical purposes one may retain the terms with $r > R_s$, assuming R_s to be the distance at which a spin S creates a local field twice as large as the observed NMR linewidth.

The results of calculations of different contributions to the second moment of ¹⁶⁹Tm NMR in TmES together with the experimental values are presented in fig. 17 (Egorov et al. 1984b). According to the EPR data the crystal under study contains Tb³⁺ ($f = 4.6 \times 10^{-4}$), Er³⁺ (4.6×10^{-4}), and Yb³⁺ (1.5×10^{-4}) ions. The most noticeable contribution to the line broadening is due to terbium ions with the largest magnetic moment ($g_{\parallel} = 17.72$); in this case the value $R_s = 20$ Å has been assumed. The contribution of crystal imperfections, calculated according to eq. (158), is shown by curve A in fig. 17. The resulting curve for M_2 is in fairly good agreement with experimental results.

The quantitative analysis reveals the origin of the surprisingly strong anisotropy of the second moment of the thulium NMR line. The small value of M_2 in the field $H_0 || c$ is

the result of switching-off of all the sources of line broadening other than dipole-dipole interactions of thulium nuclei with each other owing to the inequality $|\gamma_{\parallel}| \ll |\gamma_{\perp}|$. The magnitude of M_2 in a field $H_0 \perp c$ at a frequency of 3.9 MHz is composed in the following manner: the interaction of the thulium nuclei with each other makes up 4% of the measured value of M_2 , the "thulium-proton" interaction makes up 56%, the "thulium-paramagnetic impurities" interaction makes up 25%, and the defects of the crystal structure make up 15%. The greater part of the linewidth is due to the scatter in the local magnetic field coming from the protons. This scatter is so large that the spin echo of thulium nuclei can be observed in a homogeneous external field (Al'tshuler et al. 1969, Aukhadeev et al. 1973, Egorov et al. 1984b). The echo signal at 7–15 MHz can be described by an exponential function, which is close to a Gaussian with the characteristic time $T_2^* = 4 \,\mu$ s. The Fourier transform of this echo signal closely coincides with the distribution function of the resonance frequencies of thulium nuclei in the local fields of the protons (Egorov et al. 1984b).

3.4. Nuclear magnetic relaxation and nuclear acoustic resonance

3.4.1. Effects of thermally excited 4f-states on NMR spectra

It has been mentioned already, that NMR spectra at heightened temperatures are modified due to the population of high-lying electronic states of the VV ions. At sufficiently large lifetimes of the excited states $|m\rangle$, supplementary absorption lines must appear at frequencies ω_m , corresponding to effective fields H_m in these states and with intensities proportional to Boltzmann factors ρ_m . In fact, the NMR frequencies occur as random time variables, and the pattern of the spectrum is determined by characteristics of the random process of the VV ion transitions between different stationary states. If only the magnitude and not the direction of the effective fields H_m changes in these transitions, the lineshape can be calculated for any value of the correlation time of the random process. This occurs, e.g., for NMR of ¹⁶⁹Tm in TmES at $H_0 || c$ (Aminov et al. 1982). In the case of two frequencies ω_0 , ω_1 and $\rho_0 = \rho_1 = \frac{1}{2}$, we deal with the conventional illustration of drawing together and subsequent confluence of two similar resonance lines when the rate of frequency exchange is increased. Arbitrary values of ρ_m have been considered by Burshtein (1968).

For a Tm³⁺ ion in TmES at not too high temperatures $(k_B T \ll \Delta)$, it is sufficient to consider three electronic states $|0\rangle$, $|d_{1,2}\rangle$ (see fig. 8) which will be numbered by indices 0, 1, 2, and whose populations evidently satisfy the conditions

$$\rho_0 \approx 1 \gg \rho_1 \approx \rho_2 \approx \exp(-\Delta/k_{\rm B}T).$$
(167)

The transition between doublet states is improbable. Indeed, the probability of spinlattice transition between close levels is small, because such a transition is due to lowfrequency phonons with small spectral density, while the transition due to dipole-dipole interactions with neighbouring ions is prohibited in the first approximation. The lifetimes of both doublet states are almost equal for the same reasons (and prove to be equal to the correlation time τ_c). Under the conditions (167) the principal maximum of the lineshape function is near ω_0 at any value of τ_c , and this function is reduced to the Lorentzian:

$$I(\omega) = \rho_1 \frac{\Gamma}{(\omega_0 - \omega + \delta \omega)^2 + \Gamma^2},$$
(168)

where

$$\delta\omega = \sum_{i=1,2} \frac{\Delta\omega_i}{1 + \Delta\omega_i^2 \tau_c^2} e^{-\Delta/kT}, \qquad \Gamma = \sum \frac{\tau_c \Delta\omega_i^2}{1 + \Delta\omega_i^2 \tau_c^2} e^{-\Delta/kT}, \tag{169}$$

and $\Delta \omega_i = \omega_i - \omega_0$. In the case of rapid fluctuations,

$$|\Delta \omega_i| \tau_c \ll 1, \tag{170}$$

and the observed resonance frequency appears equal to the sum of resonance frequencies in all electronic states weighed with the Boltzmann factors, i.e., it is expressed through the paramagnetic susceptibility. This is the basis for using the proportionality relation $a \propto \chi^T$ between the paramagnetic shift tensor and the temperature-dependent susceptibility. The agreement with experimental results of lineshifts calculated in such a way (see fig. 13a, above) indicates that fast fluctuations (eq. 170) take place in this case. The line broadening obtained from the theory is in good agreement with experiment, if we use the value $\tau_c = 3.4 \times 10^{-10}$ s for the correlation time, which does not violate the rapid-fluctuation condition.

The lifetime of the excited states of a Tm³⁺ ion is determined by the spin-lattice relaxation processes and by an excitation energy transfer to neighbouring thulium ions due to interionic interactions. In order to estimate the probability of an ion transition to the ground state with a spontaneous emission of a phonon with energy Δ , we make use of the experimental data on electron spin-lattice relaxation of Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺ ions in LaCl₃, LaES and LaMgN (lanthanum magnesium nitrate) crystals, published by Al'tshuler and Kozyrev (1972). In these crystals the lowest excited levels of 4f electrons are separated from the ground doublets by an interval $\Delta = 44-48$ K, close to that for a Tm³⁺ ion in TmES. The rates of a two-phonon resonance fluorescence-type relaxation are equal, $T_1^{-1} = -w \exp(-\Delta/k_B T)$, and for all the mentioned crystals the pre-exponential factor w (which approximately coincides with the probability of the spontaneous transition of an ion to the ground state) occurs within the limits 6×10^8 to $4 \times 10^9 \text{ s}^{-1}$, which corresponds to the average lifetime $\tau \approx 5 \times 10^{-10}$ s of an excited state.

The spin-spin relaxation mechanism shortens the obtained lifetime by approximately an order of magnitude. Let \mathcal{H}_l be a Hamiltonian of an ion interaction with the *l*-th neighbouring ion; $(\mathcal{H}_l)_{mn}$ is a matrix element of the energy E_m transfer from an ion to the *l*-th neighbour, $|n\rangle$ being either of the excited states $|d_{1,2}\rangle$ of the neighbour. Then the rate of the excitation departure from the ion is written as

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_{l,n} \left| (\mathcal{H}_l)_{mn} \right|^2 g(\omega_{mn}).$$
(171)

Here $g(\omega)$ is a form factor which takes into account the finite width of the energy levels, and ω_{mn} is the frequency detuning between the excited states, equal either to 0 or Ω . Supposing the level broadening is due just to interionic interactions, one may choose $g(\omega)$ to be a Lorentzian function

$$g(\omega) = \frac{\tau}{\pi (1 + \omega^2 \tau^2)}.$$
(172)

In ethylsulfates the lanthanide ions are separated by comparatively large distances, so the long-range dipole–dipole and via-phonon-field interactions are the most important ones. An estimate of the lifetime of the excited doublet of the thulium ion due to $\mathcal{H}_{dip-dip}$, according to eqs. (171) and (172), gives the value $\tau_c = 5 \times 10^{-11}$ s. Some dependence of τ_c on the orientation of the applied field is connected with the change of the doublet splitting Ω (the value ω_{mn} in eq. 171): it is considerably larger for the parallel than for the perpendicular orientation, so the excitation energy is transferred to a similar state of the other ion with the same energy (in the second case the energy may be transferred to both excited states).

We see that spin-lattice and spin-spin relaxation processes involve very small correlation times of random processes of activation-deactivation of the VV ions, which supports condition (170).

3.4.2. Nuclear relaxation mechanisms

In general, the effective magnetic field on a nucleus, fluctuating due to transitions of VV ions between different electronic states, has components perpendicular to a nuclear spin quantization axis (Z) and therefore results in nuclear spin-lattice relaxation. Under conditions (170) of rapid fluctuations of the nuclear surroundings, Bloembergen et al. (1948), Wangsness and Bloch (1953) and Redfield (1957) have developed a theory of nuclear relaxation. For the simplest case of spin $I = \frac{1}{2}$, this theory is reduced to the basis of the phenomenological Bloch equations (Bloch 1946) and to the calculation of the relaxation parameters T_1 and T_2 . The Hamiltonian of a spin-system is written as

$$\mathcal{H} = -\gamma \hbar I [H + h(t)], \qquad (173)$$

where H is the effective field at the spin site, and h(t) is a fluctuating field, which is a random time variable. Then (Aminov et al. 1984):

$$T_1^{-1} = j_{XX}(\omega_0) + j_{YY}(\omega_0), \qquad T_2^{-1} = T_1^{-1} + j_{ZZ}(0), \tag{174}$$

where

$$j_{qq}(\omega) = \operatorname{Re} \gamma^2 \int_0^\infty d\tau \,\overline{h_q(\tau) h_q(0)} \, \mathrm{e}^{\mathrm{i}\omega t}, \qquad (175)$$

in which the overline indicates an average over the ensemble of random variables, and ω_0 is the resonance frequency. If $I > \frac{1}{2}$, formulae (174) and (175) can be used as crude estimates of the spin-lattice relaxation rate and the relaxation broadening of a resonance line.

The nucleus of the VV ion is most sensitive to fluctuations of the hyperfine magnetic field; in this case

$$\boldsymbol{H} = \boldsymbol{H}_{0} - \left(\frac{A_{\mathrm{J}}}{\gamma\hbar}\right) \langle \boldsymbol{J} \rangle_{0}, \qquad \boldsymbol{h}(t) = -\frac{\boldsymbol{J}(t) - \langle \boldsymbol{J} \rangle_{0}}{\gamma\hbar}, \tag{176}$$

where the quantity J(t) is determined instantly by the corresponding "stationary" state of the ion, and $\langle \cdots \rangle_0$ means averaging with an equilibrium electronic density matrix of the ion.

For nuclei of diamagnetic ligands, coupled to paramagnetic centers by dipole-dipole interactions,

$$\boldsymbol{h}(t) = -\sum \frac{g_{\mathrm{J}}\mu_{\mathrm{B}}}{r^{3}} \left\{ \left[\boldsymbol{J}(t) - \langle \boldsymbol{J} \rangle_{0} \right] - \frac{3}{r^{2}} \boldsymbol{r} \left(\left[\boldsymbol{J}(t) - \langle \boldsymbol{J} \rangle_{0} \right] \boldsymbol{r} \right) \right\},$$
(177)

with the summation over the ions surrounding the nucleus. A similar fluctuating field brings about the relaxation of impurity paramagnetic centers in VV paramagnets.

Dipolar fields on a nucleus fluctuate not only because of the random changes of the moment J(t), but also as a result of the change in distance r between the nucleus and the paramagnetic ion at thermal vibrations of a lattice ["Waller's" relaxation mechanism, cf. Waller (1932)]. The Hamiltonian of interaction to first order in deformation may be written as $\mathcal{H}_1(t) = -\gamma \hbar I h(t)$, where

$$h_{\alpha}(t) = g_{\mathrm{J}}\mu_{\mathrm{B}} \sum_{i} \frac{1}{r_{0}^{3}} G_{i}^{\alpha\beta} J_{\beta} e_{i}, \qquad (178)$$

and e_i are linear combinations of the nonsymmetrized tensor $u_{\alpha\beta}$ (**u** is a displacement vector; cf. eq. 10), which transform under rotations as real spherical functions:

$$e_{1} = \frac{1}{\sqrt{3}}(u_{xx} + u_{yy} + u_{zz}), \qquad e_{2} = \frac{1}{\sqrt{6}}(2u_{zz} - u_{xx} - u_{yy}),$$

$$e_{3} = \frac{1}{\sqrt{2}}(u_{xx} - u_{yy}), \qquad e_{4} = \frac{1}{\sqrt{2}}(u_{yz} + u_{zy}), \qquad e_{7} = \frac{1}{\sqrt{2}}(u_{yz} - u_{zy}).$$
(179)

The components e_5 , e_6 and e_8 , e_9 can be obtained from e_4 and e_7 , respectively, by cyclic permutation of indices x, y, z. Structural factors $G_i^{\alpha\beta}$, arising at the expansion of

380

dipole-dipole interactions, are composed of direction cosines of an equilibrium distance, $n_{\alpha} = r_{0\alpha}/r_0$; for instance, $G_1^{\alpha\beta} = (-\sqrt{3})(\delta_{\alpha\beta} - 3n_{\alpha}n_{\beta})$, etc. The role of fluctuating parameter in eq. (178) is played by the deformation e.

The crystal potential of a VV ion is also changed occasionally under thermal vibrations, which, in turn, results in nndom changes of the paramagnetic shift a and the quadrupolar interaction in eq. (134). To first approximation in e, the electron-deformation interaction equals $\sum V_i e_i$ and therefore the effective Hamiltonian of the spin-phonon interaction is

$$\mathcal{H}' = \sum \left[G_{\alpha\beta i} (I_{\alpha} H_{\beta} + I_{\beta} H_{\alpha}) + P_{\alpha\beta i} I_{\alpha} I_{\beta} \right] e_{i}, \tag{180}$$

where

$$G_{\alpha\beta i} = g_{J}\mu_{B}A_{J}\left(\left\langle 0 \middle| J_{\alpha}C_{0}V_{i}C_{0}J_{\beta} + J_{\alpha}C_{0}J_{\beta}C_{0}V_{i} + V_{i}C_{0}J_{\alpha}C_{0}J_{\beta} \middle| 0 \right\rangle - \left\langle 0 \middle| V_{i} \middle| 0 \right\rangle \left\langle 0 \middle| J_{\alpha}C_{0}J_{\beta} \middle| 0 \right\rangle\right),$$

$$(181)$$

in which energies and wave functions are taken in the zeroth order in deformation. The tensor $P_{\alpha\beta i}$ looks similar: only the hyperfine interaction parameter A_J appears, instead of $g_J\mu_B$, in eq. (181). If the spin $I = \frac{1}{2}$, there is no term with $P_{\alpha\beta i}$ in eq. (180), however, even for $I > \frac{1}{2}$ at usual magnetic fields, this term is of the same order of magnitude as the first one, unlike the case of electronic spin-lattice relaxation. In the usual NMR the considered relaxation mechanism is inessential, but for the VV ion nuclei, coupled to the crystal field much more effectively, this mechanism may be manifested at very low temperatures, when other mechanisms are "frozen out". Evidently, the first term in eq. (180) may be presented in the form of eq. (173). In fact, the value T_1^{-1} in eq. (174) equals the sum of probabilities per unit time of nuclear spin transitions between stationary states $|+\rangle$ and $|-\rangle$. Therefore, in the case of relaxation mechanisms with the help of phonons one may use the result of the conventional calculation of such probabilities between any spin states $|i\rangle$ and $|f\rangle$ (Aminov 1978, Aminov and Teplov 1990):

$$T_{1}^{-1} = w_{if} + w_{fi} = \frac{1}{6} \frac{\omega_{0}^{3}}{\pi \hbar dv_{m}^{5}} \operatorname{cotanh} \frac{\hbar \omega_{0}}{2k_{\mathrm{B}}T} \sum_{i} q_{i} |\langle i| U_{i} |f\rangle|^{2}, \qquad (182)$$

where

$$v_m^{-5} = \frac{2}{5}(v_l^{-5} + \frac{3}{2}v_t^{-5}), \qquad q_1 = \left(\frac{v_m}{v_l}\right)^5, \qquad q_{2-6} = 1, \qquad q_{7-9} = \left(\frac{v_m}{v_t}\right)^5,$$
(183)

 v_l , v_t are longitudinal and transverse sound velocities. Operators U_i are defined by equation $\mathcal{H}_1 = \sum U_i e_i$, and for the mechanisms considered above, their form is determined from eqs. (178) or (180). A separate probability of a transition with a phonon absorption (or emission) is obtained from eq. (182) by substituting $n_{\omega 0} = [\exp(\hbar \omega_0 / k_B T) - 1]^{-1}$ (or

Table 15 Some experimental data on spin-lattice relaxation of ¹⁴¹Pr and ¹⁶⁹Tm nuclei in dielectric VV paramagnets $(T_1^{-1} = A \exp(-\Delta'/k_BT))$

Crystal	Ref.	Temperature (K)	Magnetic field orientation	A (s ⁻¹)	Δ' (cm ⁻¹)
Pr ₂ (SO ₄) ₃ ·8H ₂ O	1	6-9.2	arbitrary	8.4×10 ⁷	55
Pr(NO ₃) ₃ ·6H ₂ O	1	3.5-5.5	arbitrary	4.0×10 ⁶	27
Pr(ReO ₄) ₃ ·4H ₂ O	1	2.5-5.2	arbitrary	2.2×10^{6}	19.7
TmES	2, 3	3.0-5.0	$H_0 \perp c$	1.8×10 ⁸	32
LiTmF₄	4	2.5-4.2	$H_0 \ c$	4.4×10 ⁶	27
TmPO₄	5	2.5-3.4	$H_0 \perp c$	3.1×10^{6}	25.6
TmVO₄	5	0.3-1.0	$H_0 \ c$	1.4×10^{4}	1.5

References

(1) Konov and Teplov (1976a)

(2) Al'tshuler et al. (1969)

(3) Aukhadeev et al. (1973)(4) Antipin et al. (1979)

 $n_{\omega 0} + 1$) for cotanh($\hbar \omega_0 / 2k_B T$). Expression (182) is obtained by use of the Debye model

(5) Suzuki et al. (1981)

for lattice vibrations.

Correlation functions for random processes (176), (177) are as follows:

$$g_q(t) = \overline{h_q(t)h_q(0)} = \operatorname{Sp}[\rho_{el}\hat{h}_q(t)\hat{h}_q(0)], \qquad (184)$$

where

$$\hat{h}(t) = \exp(-\frac{i}{\hbar}\mathcal{H}_{el}t)\,\hat{h}\exp(\frac{i}{\hbar}\mathcal{H}_{el}t),$$

 \mathcal{H}_{el} is the energy of a VV ion plus its interactions with the lattice, and ρ_{el} is the corresponding density matrix. For the model three-level systems (e.g., Tm³⁺ in TmES) the calculation of the $g_q(t)$ is simplified due to the presence of the characteristic time τ_c . The single-ionic Hamiltonian is substituted for \mathcal{H}_{el} ,

$$\mathcal{H}_{el} = \mathcal{H}_0 + g_J \mu_B \boldsymbol{H}_0 \boldsymbol{J}, \tag{185}$$

and the damping is taken into account in a semi-phenomenological manner, by introducing the factor $\exp(-t/\tau_c)$ into the right-hand side of eq. (184). After diagonalizing the matrix \mathcal{H}_{el} in the space of doublet states, we obtain the following comparatively simple formulae for relaxation rates of the nuclei of the VV ions:

$$\frac{1}{T_{1}} = \frac{2A_{J}^{2}\tau_{c}}{\hbar^{2}}\sin^{2}\theta'\left\{a^{2} + b^{2}\omega_{0}^{2}\left(9\cos^{2}\theta' + \frac{1+\cos^{2}\theta'}{1+\Omega^{2}\tau_{c}^{2}}\right)\right\}\exp\left(-\frac{\Delta}{k_{B}T}\right), \quad (186)$$

$$\frac{1}{T_{2}} = \frac{1}{2T_{1}} + \frac{2A_{J}^{2}\tau_{c}}{\hbar^{2}}\left\{a^{2}\cos^{2}\theta' + b^{2}\omega_{0}^{2}\sin^{4}\theta'\left(9 + \frac{1}{1+\Omega^{2}\tau_{c}^{2}}\right)\right\}\exp\left(-\frac{\Delta}{k_{B}T}\right), \quad (187)$$

where $a = \langle d_1 | J_z | d_1 \rangle$, $b = 2g_J \mu_B \langle d_1 | J_x | \theta \rangle^2 / \gamma_\perp \Delta$, Ω is a doublet splitting which may include a small initial splitting Ω_0 ($\Omega_0 \tau_c \ll 1$), and the angle θ' is defined by the orientation of the applied field (see eq. 138).



Fig. 18. Angular dependence of the spin-lattice relaxation rate of the ¹⁶⁹Tm nuclei in TmES (Aminov et al. 1984) at 4.2 K, and resonance frequencies 7.5 MHz ($\theta \le 50'$) and 13 MHz ($\theta \ge 3^\circ$). The curve is calculated using eqs. (186) and (171).

The exponential dependence on inverse temperature, predicted by eqs. (186) and (187), is characteristic of the spin-lattice relaxation of nuclei of lanthanide ions in the VV paramagnets in a certain temperature region. Some experimental results on nuclear relaxation, induced by hyperfine magnetic field fluctuations, are given in table 15.

The strong anisotropy of the spin-lattice relaxation at near parallel orientations of an applied field H_0 , which follows from eq. (186) (the factor $\sin^2 \theta'$), has been observed in TmES (fig. 18) (Aminov et al. 1984). An increase of the relaxation rate at a θ -change from 90° to 7.5° may be due only to the increase of the correlation time τ_c . As mentioned above, the dependence $\tau_c(\theta)$, is due to the broadening of the doublet level of thulium ion by interionic interactions.

In the closely parallel orientation $H_0 || c$ small transverse components of the hyperfine field, which induce relaxation transitions, can also occur as a consequence of the local distortion of a crystal field symmetry (e.g., near impurity ions; see sect. 3.5). In insufficiently perfect crystals this effect can almost entirely conceal the sharp dip in T_1^{-1} in the vicinity of $\theta = 0$, which apparently is what occurs in LiTmF₄ (Aminov et al. 1980).

The quantity T_2^{-1} is a part of the line width, which is due to the fluctuational mechanism and is designated as Γ in eq. (168). Its value does not depend on the resonance frequency ω_0 at parallel orientation; at other orientations that dependence has an approximate form $T_2^{-1} = c' + c'' v^2$. The measurements in TmES at high frequencies (v > 20 MHz) confirm the expected dependence (fig. 19). At low frequencies the temperature-dependent broadening is small, and the lineshape is strongly deflected from the Lorentzian.



Fig. 19. Pre-exponential factor A_{θ} of the relaxation rate of the transverse magnetization of the ¹⁶⁹Tm nuclei in TmES as a function of the square of the resonance frequency v^2 (Aminov et al. 1983, 1984).

The correlation function (184) for the random dipolar fields (177) is calculated in much the same way. For the model three-level system (fig. 8) we write down the relaxation rates for nuclei of diamagnetic ligands at $H_0 || c$ as follows:

$$T_{1}^{-1} = 18\gamma_{1}^{2}g_{J}^{2}\mu_{B}^{2}\tau_{c}a^{2}\sum_{i}r_{i}^{-6}\sin^{2}\theta_{i}\cos^{2}\theta_{i}\exp(-\Delta/k_{B}T),$$

$$T_{2}^{-1} = \gamma_{1}^{2}g_{J}^{2}\mu_{B}^{2}\tau_{c}a^{2}\sum_{i}r_{i}^{-6}\left[\sin^{2}\theta_{i}\cos^{2}\theta_{i} + 2(1-3\cos^{2}\theta_{i})^{2}\right]\exp(-\Delta/k_{B}T),$$
(188)

where θ_i is an angle between the *c*-axis and the radius-vector \mathbf{r}_i , connecting the nucleus with the *i*-th VV ion. Experimental values of T_1 for ¹⁹F nuclei in LiTmF₄ (Antipin et al. 1979) as well as results of the calculation are given in fig. 20. Calculations were made using eq. (188) with $\tau_c = 1.2 \times 10^{-11}$ s, which value is found from eq. (171) for the probability of dipole-dipole transfer of an excitation from an ion to neighbouring ions. The relaxation rates of the fluorine nuclei are much less than that of the thulium nuclei since the hyperfine field of 4f-electrons is essentially greater than the dipolar field on a fluorine nucleus. At the same time this rate appreciably exceeds the fluorine nuclei relaxation rate in diamagnetic crystals (cf. Abragam 1961).

The effectiveness of the relaxation processes with thermal excitations of electronic states of the matrix ions diminishes as $\exp(-\Delta/k_B T)$ with the decrease of temperature. At fairly low temperatures the mechanism of nuclear relaxation via impurity paramagnetic centers, common for dielectrics, comes into effect (Abragam 1961, Khutsishvili 1968, Atsarkin 1980). This is well illustrated in fig. 20: the temperature motion of the nuclear relaxation rate is sharply slowed down for ¹⁹F at T < 5 K and for ¹⁶⁹Tm at T < 3 K, and at the lowest temperatures the thulium nuclear moments relax only ten times faster than those of fluorine. This fact clearly shows that the relaxation of different nuclei proceeds by a single channel. The observed factor-of-ten difference is easily obtained, if one multiplies the concentration ratio $n_{\text{Tm}}/n_F = \frac{1}{4}$ by the ratio of the squares of their magnetic moments $\gamma_{\text{Tm}}^2/\gamma_F^2 = 36$. Thus, the role of 4f electrons is reduced here to the enhancement of dipole–dipole interactions of nuclei of the VV ions with impurity paramagnetic centers.



Fig. 20. Spin-lattice relaxation rate of the ¹⁶⁹Tm (circles) and ¹⁹F (triangles) nuclei in LiTmF₄ with an Er³⁺ ion impurity (relative concentration 10^{-4}) as a function of the inverse temperature (Antipin et al. 1979). The external field H_0 is parallel to the *c*-axis, the resonance frequency is 10.6 MHz; the dashed line is the calculated relaxation rate of the ¹⁹F nuclei.

For very low temperatures $(k_BT \ll g_{\parallel}\mu_BH_0)$, where an electronic polarization of impurity ions becomes significant, the efficiency of the relaxation mechanism discussed here will once again decrease sharply. It is precisely this phenomenon which gives rise to the well-known "freeze-out" effect of nuclear polarization (Borghini 1966). In this case, evidently, the nuclear spin-lattice relaxation comes about via direct energy transfer from the spins to the lattice, due to the relaxation transitions between nuclear sublevels with emission or absorption of a phonon of the corresponding frequency. The effective Hamiltonian of the spin-phonon interaction has the form (180), and the rate of relaxation transitions, with the Debye model for lattice vibrations, can be written down in the standard form (182), where *i* and *f* now designate the nuclear sublevels. A similar expression is obtained when we calculate the relaxation rate for transitions between the *i* and *f* states of the electronic Kramers doublet due to the electron-deformation interaction. The only difference between the nuclear and electronic situations involves the resonance frequency, thus one can write (Abragam and Bleaney 1983):

$$\frac{1}{T_{\text{lnucl}}} \approx \frac{1}{\tau_1} \left(\frac{\omega_{\text{nucl}}}{\omega_{\text{el}}}\right)^5 \operatorname{cotanh}\left(\frac{\hbar\omega_{\text{nucl}}}{2k_{\text{B}}T}\right) \tanh\left(\frac{\hbar\omega_{\text{el}}}{2k_{\text{B}}T}\right),\tag{189}$$

where τ_1 is the electronic spin-lattice relaxation time of Kramers lanthanide ions with splittings comparable to Δ in a crystal field, which are embedded in the host matrix with the appropriate density and sound velocity.

The relaxation mechanism under discussion is very weak. According to the calculation of Vaisfel'd (1972), the relaxation time for ¹⁶⁹Tm nuclei in TmES for a temperature of 4.2 K in a field of 500 Oe perpendicular to the *c*-axis of the crystal, must be of the order of 10^{11} s. However the probability of a direct relaxation transition grows with the increasing magnetic field as H_0^4 . Assuming $H_0 = 80$ kOe, we obtain $T_1 = 150$ s at T = 4.2 K and 9 hours at 0.02 K. Clearly, these estimates contribute to the idea of cooling the spin-system of nuclei of the VV ions to ultralow temperatures by "brute force" techniques.

However, investigation of the spin-lattice relaxation of thulium nuclei in TmES at ultralow temperatures (70–100 mK) and strong magnetic fields (up to 60 kOe) revealed that the relaxation is not exponential and the relaxation rate, large enough as it is, does not depend on magnetic field magnitude and temperature (Volodin et al. 1986). At the same time the equilibrium magnetization of the ¹⁴¹Pr nuclei in Pr₂(SO₄)₃.8H₂O at T = 80 mK is established according to an exponential law with the rate $T_1^{-1} = 6.9 \times 10^{-25} H_0^4 \text{ s}^{-1}$. A minimum of $T_1 \approx 100$ hours has been found at T = 80 mK and $H_0 = 47$ kOe. Roinel et al. (1985) have studied the longitudinal magnetization relaxation of ¹⁶⁹Tm nuclei in a TmPO₄ single crystal at 50 mK. They found that with increasing magnetic field perpendicular to the *c*-axis, the relaxation time T_1 at first grows sharply (from 40 s at 350 Oe to 3×10^6 s at 5 kOe), and then begins to decrease approximately as $1/H_0$, reaching a value of 3×10^5 s at $H_0 = 55$ kOe. The observed nonexponential character of the ¹⁶⁹Tm nuclear relaxation at strong fields was ascribed to the presence of the phonon bottle-neck in direct processes of nuclear relaxation.

The method of nuclear acoustic resonance proves to be suitable for studying the nuclear spin-phonon interaction using a moderate magnetic field. Resonance absorption of the ultrasound can be regarded as the phenomenon inverse to magnetic relaxation through one-phonon processes (Al'tshuler and Kozyrev 1972). Therefore the considerations discussed earlier are also relevant to estimates of the magnitude of sound absorption by nuclei of the VV ions. The absorption coefficient of sound due to transitions between nuclear sublevels i, f takes the form of

$$\sigma_{if} = \left(\frac{\pi n\omega_0}{\hbar d\nu^3}\right) g(\omega) \tanh\left(\frac{\hbar \omega_0}{k_{\rm B}T}\right) \left|\sum_i \langle i | U_i | f \rangle (\boldsymbol{e}_1 \boldsymbol{\lambda})_i\right|^2,$$
(190)

where *n* is the nuclear concentration, $g(\omega)$ is the form factor of the NMR line normalized to unity; e_1 is a unit polarization vector, $\lambda = q/q$ is a unit wave vector, and the quantities $(e_1\lambda)_i$ are defined in analogy with eq. (179). Due to the high concentration of absorbing centers and the frequency, which is large compared to the usual one in NMR, the magnitudes of the coefficients σ_{if} are wholly measurable in experiments. The nuclear acoustic resonance in VV paramagnets was first observed on the ¹⁴¹Pr nuclei $(I = \frac{5}{2})$ in PrF₃ (Al'tshuler et al. 1979). The measurements were performed at a temperature of 4.2 K with the longitudinal ultrasound of frequencies from 21 to 36 MHz. An estimate of the absorption coefficient gave a value $\sigma \approx 10^{-6} \text{ cm}^{-1}$. Strong resonance absorption $(\sigma \approx 3 \text{ cm}^{-1} \text{ for } T = 1.6 \text{ K})$ of longitudinal acoustic waves with a frequency of 800 MHz in the HoVO₄ single crystal was observed by Bleaney et al. (1983a, 1988a). By studying resonance absorption of sound in various propagation directions and polarizations practically all the spin-phonon interaction constants, and with them the reliable estimates of the one-phonon relaxation rates of the VV ion nuclei, can be obtained.

3.5. Influence of point defects on local magnetic properties

3.5.1. EPR of impurity paramagnetic ions

Like other dielectric crystals, VV paramagnets with impurity paramagnetic ions were widely investigated. The most obvious manifestation of magnetism of an impurity center environment is a shift of the electronic g-factor, similar to the paramagnetic shift of ligand NMR discussed earlier. It is this shift which was observed by Hutchings and Wolf (1963) in their first investigation of the EPR of impurity ions Yb^{3+} in the VV paramagnets – garnets TmAlG and TmGaG. These authors proposed to use the effect for estimating the exchange interactions between impurity and host lanthanide ions. Rimai and Bierig (1964) investigated the EPR and spin-lattice relaxation of Fe³⁺ ions in thulium garnets; they observed the relaxation of impurity ions via matrix lanthanide ions. The mechanisms of this relaxation will be discussed in greater detail below.

The shift of the resonance lines in magnetic media is due not only to exchange and magnetic dipolar interactions with the nearest surroundings of an impurity ion (i.e., to the molecular field), but also to the Lorentz field and sample-shape-dependent demagnetizing field. Therefore it becomes possible to obtain the Van Vleck susceptibility by studying the dependence of the position of EPR lines of impurity ions on sample shape; this was realized, in particular, for TmGaG (Hodges 1975a) and LiTmF₄ (Korableva et al. 1982).

Various extensive EPR investigations of impurity S-state ions in VV paramagnets were carried out by Mehran et al. (1977, 1979a,b, 1980, 1982, 1983) (see also the review by Mehran and Stevens 1982). Besides g-factor shifts they considered the change of the crystal field potential on the impurity, caused by interaction with VV ions ("pseudocrystalline" contributions to the potential), and also the broadening of EPR lines. There are some sources of line broadening in VV paramagnets, besides the common ones, namely, the broadening due to magnetic and exchange interactions of the impurity with VV ions, fluctuational broadening connected with relaxation transitions of VV ions between stationary states, and indirect ("enhanced") hyperfine interactions of impurity electrons with nuclei of VV ions.

In general, calculating the above effects is like deducing the effective nuclear spin Hamiltonian, described in sect. 3.1. The Hamiltonian of interaction of an impurity ion with surrounding VV ions is written in the general form

$$\mathcal{H}_{\rm imp-VV} = \sum_{i} a^{i}_{\alpha\beta} S_{\alpha} J^{(i)}_{\beta}, \qquad (191)$$
where S is the effective spin of the impurity ion and index *i* enumerates VV ions. Including this interaction, together with the Hamiltonian \mathcal{H}' (eq. 126), into the standard procedure of the perturbation theory, we obtain appropriate corrections to the spin Hamiltonian \mathcal{H}_{imp}^{0} , which contain the interaction parameters $a_{\alpha\beta}^{i}$. At low temperatures the result is reduced to substitution of operators $J_{\beta}^{(i)}$ in eq. (191) by their average values in the ground states, and the interaction itself occurs as a correction to the Zeeman Hamiltonian of the impurity ion:

$$\mathcal{H}_{\rm imp-VV} = \Delta g_{\alpha\beta} \mu_{\rm B} S_{\alpha} H_{\beta}, \qquad \Delta g_{\alpha\beta} = -g_{\rm J} \sum_{i} a^{i}_{\alpha\gamma} T^{(i)}_{\gamma\beta}. \tag{192}$$

At higher temperatures the excited states also contribute to the average values, so the corrections become temperature-dependent, similar to the case of nuclear spin Hamiltonians (see sect. 3.3.1).

The g-factor shift may be found experimentally by comparing the EPR spectra of an impurity ion in a VV paramagnet and in analogous diamagnetic lattices. Aminov et al. (1990a) obtained the Δg_{\parallel} and Δg_{\perp} values for Ce³⁺, Nd³⁺, Dy³⁺, Er³⁺, Yb³⁺ ions in LiTmF₄, when comparing the spectra of these ions with those in LiYF₄ and LiLuF₄. The contribution of dipole-dipole interactions is calculated easily, since

$$(a_{\alpha\beta}^{i})_{\rm dip} = \left(\frac{g_{\rm J}\mu_{\rm B}^{2}}{r_{i}^{3}}\right)(g_{\alpha\beta} - 3g_{\alpha\gamma}n_{\beta}^{i}n_{\gamma}^{i}),$$

where $g_{\alpha\beta}$ are the *g*-factors of the impurity. In the estimation, allowance must be made for the difference between the crystal field Hamiltonian $\mathcal{H}_0^{(i)}$ of a VV ion and the corresponding Hamiltonian in a regular lattice due to local defectiveness of a crystal near the impurity site (more details are given in the following subsections). The part of $\Delta g_{\alpha\beta}$ which remains after subtraction of the dipolar contribution is attributed to exchange interactions with the nearest VV ions. Parameters of exchange interactions, obtained in such a way, are of the order of (or exceed) the dipole–dipole part. Thus, for Ce³⁺:

$$(a_{xx} + a_{yy})_{dip} = 1.6 \times 10^{-2} \,\mathrm{cm}^{-1}, \qquad a_{zz, \,dip} = -2.98 \times 10^{-2} \,\mathrm{cm}^{-1},$$

while

$$(a_{xx} + a_{yy})_{ex} = 1.65 \times 10^{-2}, \qquad a_{zz,ex} = -14.4 \times 10^{-2} \text{ cm}^{-1}, \quad \text{etc.}$$

These conclusions are analogous to those made by Mehran and Stevens (1982).

The lanthanide impurity ions can serve as probes of magnetic field-induced deformations of the VV paramagnets. As the magnetostriction is a nonlinear function of the magnetic field, it manifests in the nonlinear magnetic properties, for example, in magnetic anisotropy. The magnetic anisotropy can be observed most clearly in the case of isotropic linear magnetic susceptibility. The EPR spectra of the Kramers ions (Yb³⁺, Er^{3+} , Dy^{3+}) in the cylindrical sample of LiTmF₄, whose generatrix is directed along the *c*-axis, are isotropic in the (001) basal plane only in the first approximation. The magnetic field induces deformations of A_g and B_g symmetry and the latter lowers the crystal field symmetry. We shall distinguish between the nonlinear response of the 4felectron shell to a magnetic field and the lattice anisotropy due to the parastriction and the internal anisotropic magnetic field. The lattice anisotropy was singled out by Al'tshuler et al. (1985) when comparing the resonance transverse fields, obtained with EPR measurements at 74 GHz and 4.2 K, for the impurity Yb³⁺, Er^{3+} , Dy^{3+} ions in the LiTmF₄ VV paramagnet and in the LiYF₄ nonmagnetic crystal. The splitting of the Kramers doublet can easily be analyzed using an effective spin Hamiltonian (see eqs. 118, 119) containing the following terms, relevant in the present case,

$$\mathcal{H}_{S} = \mu_{B} \left\{ g_{\perp} \left(H_{x}S_{x} + H_{y}S_{y} \right) + g_{31} \left[S_{x}H_{x} \left(H_{x}^{2} - 3H_{y}^{2} \right) + S_{y}H_{y} \left(H_{y}^{2} - 3H_{x}^{2} \right) \right] \right. \\ \left. + g_{32} \left[S_{y}H_{x} \left(H_{x}^{2} - 3H_{y}^{2} \right) - S_{x}H_{y} \left(H_{y}^{2} - 3H_{x}^{2} \right) \right] \right. \\ \left. + \left(H_{x}S_{x} - H_{y}S_{y} \right) \sum_{i} \left[G_{1i}(\Gamma_{2}) e(B_{g}^{i}) + G_{1i}^{\prime}(\Gamma_{2}) \Delta w(B_{g}^{i}) \right] \right. \\ \left. + \left(H_{x}S_{y} - H_{y}S_{x} \right) \sum_{i} \left[G_{2i}(\Gamma_{2}) e(B_{g}^{i}) + G_{2i}^{\prime}(\Gamma_{2}) \Delta w(B_{g}^{i}) \right] \right\}.$$

$$(193)$$

In contrast with eq. (118), this expression contains additional terms which are nonlinear in the magnetic field and are obtained in the third order in \mathcal{H}_Z . In analysis of experimental data, the local magnetic field H of the cylindrical sample affecting the impurity ion, considered up to third order in the external field $H_0 = H_0(\cos \varphi, \sin \varphi, 0)$, should be inserted into eq. (193). When neglecting the exchange interactions,

$$H = \alpha_1 H_0 + \alpha_3 H_0^3 \cos [4(\varphi - \varphi_0)],$$

where $\alpha_1 = 0.973$, $\alpha_3 = -2.661 \times 10^{-6}$ (kOe)⁻², $\varphi_0 = 12.2^\circ$, and the nonlinear isotropic terms are omitted. After substituting into eq. (193) the characteristics of the field-induced lattice deformation $e(B_g^i|H_0)$ and $\Delta w(B_g^i|H_0)$ which were described in sect. 3.2, we find the splitting of the doublet

$$\Delta \varepsilon = \mu_{\rm B} \left\{ \alpha_1 g_\perp + A H_0^2 \cos \left[4(\varphi - \varphi_{\rm g}) \right] \right\} H_0. \tag{194}$$

The anisotropy constant A and the angle φ_g specifying the direction of the extreme resonant field in the (001) plane can be easily written through the parameters of the intrinsic anisotropy (g_{3i}) of the doublet, the spin-phonon coupling constants $[G_{ij}(\Gamma_2),$ $G'_{ij}(\Gamma_2)]$ and the constant of the local field anisotropy (α_3). The results of calculations (given in parentheses below) of the g-factor anisotropy in the LiTmF₄ crystal agree well enough with the experimental data: A = 13 (12.5) for Yb³⁺, 380 (398) for Er³⁺ and 1640 (860) for Dy³⁺ in units of 10⁻⁶ (kOe)⁻². The proper magnetic anisotropy of the

Ion	Crystal	$g_x(g_\perp)$	$g_y(g_\perp)$	$g_z(g_{\parallel})$	Reference
Ce ³⁺	EuES	0.2	0.2	3.785	Nejlo and Prokhorov (1983)
	LiTmF₄	1.373	1.373	2.767	Aminov et al. (1989)
	PrF ₃	0.39	0.946	2.69	Rachford and Huang (1971)
Nd ³⁺	$Eu_3Ga_5O_{12}$	3.820	1.965	1.190	Hodges (1975b)
	TmES	1.956	1.956	3.69	Aminov et al. (1986)
	LiTmF₄	2.611	2.611	2.06	Aminov et al. (1989)
	PrF ₃	1.500	1.094	2.933	Rachford and Huang (1971)
Dy ³⁺	LiTmF₄	9.476	9.476	1.183	Aminov et al.(1989)
	Cs ₂ NaHoCl ₆ ^a				Bleaney et al. (1981b)
Er ³⁺	TmES	8.732	8.732	1.521	Aminov et al. (1986)
	LiTmF₄	8.074	8.074	2.960	Antipin et al. (1979)
		7.586	7.586	2.959	Aminov et al. (1989)
	PrF ₃	2.801	4.48	11.36	Rachford and Huang (1971)
Yb ³⁺	$Tm_3Al_5O_{12}$	2.559	3.742	3.998	Hodges (1978)
		2.55	3.75	4.02	Hutchings and Wolf (1963)
	$Tm_3Ga_5O_{12}$	2.94	3.56	3.72	Hutchings and Wolf (1963)
	$Eu_3Ga_5O_{12}$	2.68	3.66	3.81	Hodges (1975b)
	LiTmF ₄	3.974	3.974	1.327	Aminov et al. (1989)
	PrF ₃	3.47	5.427	1.205	Rachford and Huang (1971)
	Cs₂NaHoCl ₆ ^b				Bleaney et al. (1981a)

 Table 16

 EPR parameters of the impurity lanthanide ions with an effective spin $S = \frac{1}{2}$ in some dielectric crystals at liquid helium temperatures

^a g = 6.60 (cubic symmetry).

^b g = 2.58 (cubic symmetry).

Yb³⁺ ion is very small due to a large gap (> 200 cm⁻¹) between the ground and nearest excited doublets, thus the isotropic EPR spectrum is observed with the magnetic field in the basal plane in LiYF₄:Yb³⁺. The clearly observed anisotropy in the EPR of the LiTmF₄:Yb³⁺ crystal is almost entirely induced by the anisotropic local magnetic field due to the VV ions. The measured relative differences between the corresponding values of the anisotropy constants A of the Dy³⁺ and Er³⁺ ions in the LiYF₄ and LiTmF₄ crystals do not exceed 20%, for these ions with small excitation energies from the ground state to the nearest sublevels (see table 5) the magnetic anisotropy is mainly an intrinsic property.

The EPR spectra of Gd^{3+} , Dy^{3+} , Er^{3+} , and Yb^{3+} ions in elpasolite $Cs_2NaHoCl_6$ were observed by Bleaney et al. (1981a). The ions were not embedded into a sample, they were there as natural impurities. No spectrum shows any deviations from the cubic symmetry in the whole temperature range investigated. The possibility to observe the EPR of the Ho³⁺ ion, whose electronic ground state is a nonmagnetic doublet, seems to be the most interesting subject here. When the magnetic field is applied, the doublet is split due to the second order Zeeman effect and the transitions between doublet states become resolved with the frequency and intensity proportional to the square of the field. A series of EPR investigations of impurity lanthanide ions, iron group and palladium group ions in thulium and europium garnets was carried out by Hodges (1975a,b, 1977, 1978, 1983a, 1985). A huge shift of the Ru^{3+} ion g-factor in $Tm_3Al_5O_{12}$ was observed due to the great enhancement of the superhyperfine interaction.

The temperature dependence of the Gd^{3+} spin Hamiltonian parameters in $PrVO_4$ and of the resonance line width was investigated by Mehran et al. (1980) and Andronenko et al. (1981). A measurement of the Tm^{3+} ion spectrum in the VV paramagnet HoND (holmium nicotinate dihydrate) should also be noted (Baker et al. 1986b). The EPR in TbND has shown a spectrum from a relatively rare species of a paramagnetic ion (defect sites) in an undiluted compound of the same paramagnetic ion (Baker et al. 1987).

Spin Hamiltonian parameters of impurity paramagnetic ions in a number of dielectric VV paramagnets are given in tables 16 and 17.

Crystal	Ref.	g-values	Fine structure parameters b_n^m (GHz)
PrCl₃·7H₂O	1	$g_x = 1.993$ $g_y = 1.958$ $g_z = 1.993$	$b_2^0 = 1.166; \ b_2^2 = -0.724$ $b_4^0 = 0.006; \ b_4^2 = -0.047; \ b_4^4 = -0.057$ $b_6^0 = 0; \ b_6^2 = -0.031; \ b_6^4 = -0.080; \ b_6^6 = -0.060$
$Pr_2(SO_4)_3 \cdot 8H_2O$	2	$g_x = 1.995$ $g_z = 1.997$	$b_2^0 = -1.863; \ b_2^2 = 1.135$ $b_4^0 = 0.035; \ b_4^2 = 0.012; \ b_4^4 = -0.016$ $b_6^0 = 0.003; \ b_6^2 = 0.014; \ b_6^4 = -0.008; \ b_6^6 = -0.001$
Pr(NO ₃) ₃ .6H ₂ O	3	$g_x = 1.997$ $g_z = 1.992$	$b_2^0 = -1.379; \ b_2^2 = 1.074$ $b_4^0 = -0.005; \ b_4^2 = -0.011; \ b_4^4 = -0.066$ $b_6^0 = 0; \ b_6^2 = 0.015; \ b_6^4 = 0.003; \ b_6^6 = 0.003$
EuES	4, 5	$g_{\parallel} = 1.99200$ $g_{\perp} = 1.99154$	$b_2^0 = 0.4998$ $b_4^0 = 0.0114$ $b_6^0 = -0.0012$
EuCl ₃ .6H ₂ O	6	$g_x = 1.9915$ $g_z = 1.9910$	$b_2^0 = 1.8754; \ b_2^2 = -1.1400$ $b_4^0 = -0.0312; \ b_4^2 = 0.0369; \ b_4^4 = 0.0041$ $b_6^0 = -0.0019; \ b_6^2 = 0.0299; \ b_6^4 = 0.0312; \ b_6^6 = 0.0144$
Eu ₂ (SO ₄) ₃ ·8H ₂ O	2	$g_x = 1.985$ $g_z = 2.005$	$b_2^0 = -1.907; \ b_2^2 = 1.082$ $b_4^0 = 0.036; \ b_4^2 = -0.005; \ b_4^4 = -0.045$ $b_6^0 = 0.003; \ b_6^2 = 0.015; \ b_6^4 = -0.018; \ b_6^6 = -0.032$
Eu(OH) ₃	7	$g_{\parallel} = g_{\perp} = 1.990$	$b_2^0 = -0.4347$ $b_4^0 = -0.0090$ $b_6^0 = 0.0018; b_6^6 = 0.018$
EuPO₄	8	g=1.991	$b_2^0 = 2.487; \ b_2^2 = 0.861$ $b_4^0 = 0.0006; \ b_4^4 = -0.147$ $b_8^0 = -0.0006$

 Table 17

 EPR parameters of impurity Gd³⁺ ions in some dielectric crystals of the Van Vleck paramagnets

Continued on next page

Crystal	Ref.	g-values	Fine structure parameters b_n^m (GHz)
$\mathrm{Eu}_3\mathrm{Ga}_5\mathrm{O}_{12}$	9	$g_x = 1.984$	$b_2^0 = 1.7847; \ b_2^2 = 1.4355$
		$g_y = 1.984$	$b_4^0 = -0.124; \ b_4^2 = 0.0070; \ b_4^4 = 0.545$
		$g_z = 1.987$	$b_6^0 = 0; \ b_6^4 = -0.0064; \ b_6^2 + b_6^6 = 0.0015$
Cs ₂ NaHoCl ₆	10	g=1.99	$b_4^0 = (-)0.052;$
			$b_6^0 = 0$ (cubic symmetry)
TmES	4, 5	$g_{\parallel} = 1.99234$	$b_2^0 = 0.4425$
		$g_{\perp} = 1.99158$	$b_4^0 = 0.0111$
			$b_6^0 = -0.0012$
TmAsO₄	11	g = 1.980	$b_2^0 = -1.053; \ b_2^2 = -0.47$
			$b_4^0 = -0.020; \ b_4^2 = 0.097$
TmVO₄	11	g = 1.970	$b_2^0 = -1.593; \ b_2^2 = -0.020$
			$b_4^0 = -0.012; \ b_4^4 = 0.11$
TmPO₄	12	g = 1.992	$b_2^0 = 2.03 \ (T = 4 \text{ K}); \ 1.95 \ (T = 150 \text{ K})$
			$b_4^0 = -0.016; \ b_4^4 = 0.40$
			$b_6^0 = 0.0014; \ b_6^4 = 0.15$

3.5.2. Spin-lattice relaxation of impurity lanthanide ions

(3) Misra and Mikolajczak (1978)

(4) Smith et al. (1977)

The relaxation mechanism, connected with the random thermal excitation of the host lanthanide ions in VV paramagnets, proves to be effective for impurity ions too. We list the results of the relaxation rate measurements for a number of impurity lanthanide ions in TmES and LiTmF₄ crystals (Aminov et al. 1986, 1989) (table 18). As for other investigations in this field, we may refer only to papers by Rimai and Bierig (1964), Rachford and Huang (1971), and Antipin et al. (1979); and only in the first of these papers was the influence of thulium ions on spin-lattice relaxation of Fe³⁺ ions in thulium garnets observed with certainty.

(11) Schwab (1975)

(12) Mehran et al. (1977)

(7) Cochrane et al. (1973)

(8) Rappaz et al. (1981)

It should be noted that the results of measurements of the Nd³⁺ spin-lattice relaxation both in TmES and LiTmF₄ depend neither on the concentration of Nd³⁺ ions, nor on the concentration of Er³⁺ ions, which have been specially embedded into the samples. The relaxation times of Yb³⁺ ions in LiTmF₄ at $H_0 || c$ and T < 3 K were shortened by the cross-relaxation through the rapidly relaxing Dy³⁺ ions (Antipin et al. 1978) present in small concentrations in the samples, since at the orientation under consideration the Zeeman splittings of Yb³⁺ and Dy³⁺ ions are very close to each other.

NONMETALLIC LANTHANIDE COMPOUNDS

Impurity ions	Field	1	$A(T) {\rm s}^{-1}$	B_1 (s ⁻¹)	Δ_1	B_2 (s ⁻¹)	Δ_2
	Orientation	Freq. (GHz)	· · ·		(cm ⁻¹)		(cm ⁻¹)
TmES (1.5–30 K)							
0.5% Nd ³⁺	$H_0 \ c$	9.4	$0.8T^{2}$	3.6×10 ⁶	32		
		24.0	30 <i>T</i>	1.25×10^{7}	32		
		36.0	160 <i>T</i>	1.25×10^{7}	32		
	$H_0 \perp c$	9.4	$1.8T^{2}$	5×10 ⁷	32		
		24.0	50 <i>T</i>	5×10 ⁷	32		
0.5% Tb ³⁺		24.0	100 <i>T</i>	7.7×10^{7}	32	7.5×10 ¹¹	100
		36.0	250 <i>T</i>	1.7×10^{7}	32	7.5×10 ¹¹	100
0.1% Er ³⁺	$H_0 \ c$	9.4	$2.2T + 10^{-3} T^9$	5.5×10^{10}	45		
	$H_0 \perp c$	9.4	$14T + 10^{-3} T^9$	8.5×10 ¹⁰	45		
		24.0	$270T + 10^{-3} T^9$	8.5×10 ¹⁰	45		
LiTmF4 (1.6–5 K)							
0.5% Ce	$H_0 \ c$	9.4	1.0 <i>T</i>	8.4×10^{6}	18.5		
		23.0	3.6 <i>T</i>	9.9×10 ⁶	18.5		
	$H_0 \perp c$	9.4	12 <i>T</i>	8×10 ⁷	18.5		
$\{0.2\%; 0.3\%; 1\%\} \text{ Nd}^{3+}$	$H_0 \ c$	9.4	1.2 <i>T</i>	9.4×10 ⁶	19.5	8.8×10 ⁸	32
		23.0	19 <i>T</i>	7×10^{6}	19.5	3.9×10 ⁸	32
	$\boldsymbol{H}_{0} \bot c$	9.4	5.9 <i>T</i>	2.9×10 ⁷	19.5	1.7×10 ⁹	32
		23.0	25T	2.3×10 ⁷	19.5		
$\{0.1\%; 0.2\%\} \mathrm{Yb^{3+}}$	$\measuredangle H_0, c = 10^{\circ}$	9.4	3 <i>T</i>	6×10 ⁸	29		
	$H_0 \perp c$	9.4	5.4 <i>T</i>	4×10 ⁸	29		
		23.0	47 <i>T</i>	6.2×10 ⁸	29		
		36.0	240 <i>T</i>	5.2×10 ⁸	29		

		Ta	ible 18				
Spin-lattice relaxation	rates of the i	impurity	lanthanide i	ons in	TmES	and LiTmF₄	crystals ^{a,b}

^a Aminov et al. (1986, 1989).

^b $(T_1^{-1})_{imp} = A(T) + B_1 \exp(-\Delta_1/k_B T) + B_2 \exp(-\Delta_2/k_B T).$

Let us compare the above results with the well-known data for diamagnetic YES, LaES (Larson and Jeffries 1966a, Marchand and Stapleton 1974, Scott and Jeffries 1962, Larson and Jeffries 1966b) and LiYF₄ (Antipin et al. 1978) crystals. The relaxation of the Er^{3+} ion in TmES differs from that in LaES but negligibly, since there is an excited level in the Stark structure of the Er^{3+} ion, which is close to the ground doublet ($\Delta = 45 \text{ cm}^{-1}$) and through which the fast two-step relaxation process proceeds. In other cases the relaxation rate of the lanthanide ions in VV paramagnets is considerably higher than in diamagnetic

crystals, the temperature dependence of the relaxation rate at higher temperatures being of exponential character, $T_1^{-1} \propto \exp(-\Delta/k_B T)$. In TmES (and in LiTmF₄ with Nd and Yb impurities) the value of $\Delta = 32 \text{ cm}^{-1}$ coincides with the least excitation energy of the Tm³⁺ ions, which bears convincing evidence to the fact that in the corresponding temperature range the relaxation is due to an interaction of the impurity ion with thulium ions.

Two relaxation mechanisms are connected with interionic interactions, the Waller mechanism and the fluctuational one, considered in detail earlier in this section for nuclear relaxation of ligands of the VV ions. Estimates of the relaxation rate, due to modulation of dipole–dipole interactions by lattice vibrations, result in $T_1^{-1} \approx 10^3 \exp(-\Delta/k_B T)$ for impurities in TmES, which is by far less than the experimental values. The relaxation rate for the fluctuational mechanism is calculated analogously to eq. (188); here the result is presented for the case of the model three-level VV ions at arbitrary orientation θ of an applied field relative to the *c*-axis:

$$T_{1}^{-1} = \frac{2a^{2}}{\hbar^{2}} \exp\left(-\frac{\Delta}{k_{\rm B}T}\right) \\ \times \sum_{i} \frac{g_{1}^{2}\mu_{\rm B}^{4}n_{i}}{r_{i}^{6}} \left[\left(1 - 3\cos^{2}\theta_{i}\right)^{2}g_{\parallel}^{2}\sin^{2}\theta' + \frac{9}{2}g_{\perp}^{2}\sin^{2}\theta_{i}\cos^{2}\theta_{i}(1 + \cos^{2}\theta')\right] \\ \times \left\{\left(1 - 4p_{1i}^{2}p_{2i}^{2}\right)\frac{\tau_{\rm c}}{1 + \omega_{0}^{2}\tau_{\rm c}^{2}} + 2p_{1i}^{2}p_{2i}^{2}\left[\frac{\tau_{\rm c}}{1 + (\Omega_{i} - \omega_{0})^{2}\tau_{\rm c}^{2}} + \frac{\tau_{\rm c}}{1 + (\Omega_{i} - \omega_{0})^{2}\tau_{\rm c}^{2}}\right]\right\},$$
(195)

where the summation is performed over VV (thulium) ion spheres, centered on an impurity ion, n_i is the number of the ions in the *i*-th sphere, r_i , θ_i are the coordinates, and Ω_i is a splitting of an excited doublet of an ion in that sphere. Coefficients p_{1i} , p_{2i} define stationary states $\psi_1(\psi_2) = p_1(p_2)|d_1\rangle + q_1(q_2)|d_2\rangle$, arising at diagonalization of the Hamiltonian (185); $\tan \theta' = (g_{\perp}/g_{\parallel})\tan \theta$, g_{\perp} , g_{\parallel} are g-factors of an impurity ion.

Apparently, eq. (195) predicts a rather complicated dependence of the relaxation rate on the magnitude and orientation of an external magnetic field, the character of these dependences being essentially determined by the values of the parameters τ_c and Ω_{0i} . For the perfect crystal without impurities $\Omega_{0i} = 0$, $p_{1i} = 0$ and neither reproduction of the experimental frequency dependence of the relaxation rate, nor satisfactory estimates of that rate by an order of magnitude can be attained. However, there are good grounds to expect a marked distortion of an axial crystal field on the Tm³⁺ ions close to the impurities, because of the mere presence of these impurities – structural defects. The quantities Ω_{0i} must essentially depend on the geometry of the coordination sphere. In TmES the thulium ions, nearest to an impurity, are on the same *c*-axis. For these ions an impurity proves to be an axial perturbation, so in this case $\Omega_{01} = 0$. The axiality of the crystal field must be distorted most strongly for the Tm³⁺ ions of the second sphere, therefore $\Omega_{02} > \Omega_{03}$. As for the correlation time τ_c , it must exceed the value of 10^{-11} s given above, since the spread of energy Δ deteriorates the conditions of resonant energy transfer between thulium ions.

$$\Omega_{01} = \Omega_{05} = 0,$$
 $\Omega_{02} = 1.17,$ $\Omega_{03} = 0.85,$ $\Omega_{04} = 0.74 \,\mathrm{cm}^{-1}.$

Moreover, supposing $\tau_c = 10^{-10}$ s, we find in accordance with eq. (195) that

$$T_1^{-1} = A(v_0) \exp(-\Delta/k_{\rm B}T),$$

the values $A(v_0, \text{ GHz})$ at $H_0 \perp c$ being equal to

$$A(9.4) = 1.07 \times 10^7$$
, $A(24.0) = 0.51 \times 10^7$, $A(36.0) = 1.31 \times 10^7 \,\mathrm{s}^{-1}$.

For parallel orientation we have

$$A(9.4) = 1.7 \times 10^5$$
, $A(24.0) = 0.94 \times 10^6$, $A(36.0) = 1.12 \times 10^7 \,\mathrm{s}^{-1}$.

These figures approximately reflect the qualitative dependencies on the frequency and orientation of an external field, observed in the experiment, and they coincide by an order of magnitude with the measured relaxation rates.

An exponential term with $\Delta \approx 30 \text{ cm}^{-1}$ in the relaxation rate of Nd³⁺ and Yb³⁺ ions in LiTmF₄ is ascribed to the fluctuational mechanism, as in the case of ethylsulfates. However, there are some specific features because of the closer arrangement of lanthanide ions in the crystal lattice. Surely, the contributions of the first and possibly second coordination spheres are eliminated from formula (195), since an alien impurity ion must give rise to a strong perturbation of an ideal crystal field at distances up to 6 Å and, consequently, to large values of Ω_{01} , Ω_{02} . Assuming $\tau_c = 5 \times 10^{-10} \text{ s}$, $\Omega_{02} = 1.23$, $\Omega_{03} = 0.8$, $\Omega_{04} = 0.36 \text{ cm}^{-1}$, for LiTmF₄:Yb³⁺ we find the following preexponential factors for various orientations and frequencies:

$$A_{\parallel}(9.4 \text{ GHz}) = 1.3 \times 10^8, \qquad A_{\perp}(9.4) = 1 \times 10^8,$$

 $A_{\perp}(23) = 1.4 \times 10^8, \qquad A_{\perp}(36) = 1.2 \times 10^8 \text{ s}^{-1},$

which almost coincides with the experimental values given in table 18.

Other exponential contributions to the relaxation rates of Ce³⁺, Nd³⁺ ions are explained naturally from the same standpoint. It seems reasonable to associate the contributions $T_1^{-1} \propto \exp(-\Delta'/k_BT)$ with $\Delta' = 18-19 \text{ cm}^{-1}$ with an influence of the thulium ions of the first coordination sphere on the impurity lanthanide ions. An impurity ion distorts the crystal field at a distance of 3.7 Å so strongly, that the thulium doublet state is split by approximately 20 cm⁻¹. In fact, there already appears a purely singlet Stark structure of energy levels in the low-symmetry crystal field. The distinction of Δ' values for different lanthanide ions can easily be connected with the distinction of differences between the ionic radii of impurities and the ionic radius of the host thulium ion. The difference is the most significant for the Ce³⁺ ion, and the "doublet splitting" $\Delta - \Delta'$ proves also to be the largest; for Yb³⁺ ion both quantities are the smallest. Singlet levels are non-magnetic, therefore the fluctuational mechanism, as described above, becomes ineffective. This is manifested formally in the relations $p_1 = p_2 = 1/\sqrt{2}$, $|\Omega_i - \omega_0| \tau_c \gg 1$ and, as a result, the T_1^{-1} value proves to be negligibly small.

To obtain reasonable estimates of T_1^{-1} , it is necessary to return to the Waller mechanism of relaxation, whose effectiveness is not connected with the presence of stationary magnetic states of the Tm³⁺ ions. Its contribution to relaxation, as mentioned above, can be appreciable in tetrafluorides due to the involvement of exchange interactions, which depend on distances much stronger than the dipole–dipole interactions. Assuming \mathcal{H}_{ex} is proportional to r^{-10} and exceeds the dipole–dipole interaction by a factor of three for the shortest interionic distance, we obtain an estimate of $T_1^{-1} \approx 10^6 \exp(-\Delta'/k_BT)$, which is close to the experimental value. The weak frequency dependence of the relaxation rate in this mechanism also corresponds to the experiment.

At low temperatures the relaxation rate becomes proportional to temperature, $T_1^{-1} \propto T$, however, in some cases it is several times greater than in the diamagnetic analogs. This excess may be partly ascribed to the difference in crystal densities and sound velocities, but the complementary one-phonon relaxation processes on the grounds of the Waller mechanism must also be taken into account. This mechanism in VV paramagnets results in the strong orientational dependence of relaxation rates, connected with the strong anisotropy of the susceptibility of the VV ions. The frequency dependence is also stronger than usual, since the magnetic moment of a VV ion itself is proportional to H_0 , i.e., to the resonance frequency ω_0 . The observed peculiarities of the low-temperature relaxation of Nd³⁺, Er³⁺, Yb³⁺ ions in LiTmF₄ have been interpreted in this way (Aminov et al. 1990a).

3.5.3. Local distortions of a crystal lattice due to impurity ions

The microscopic model, elaborated for the interpretation of the spin-lattice relaxation measurements, ascribe the observed values of Δ' to the Stark structure of the host lanthanide (thulium) ions which experience the largest perturbation under the implantation of the impurities. For further verification of this assumption, the optical absorption spectra of Tm³⁺ ions were investigated both in pure (undoped) and doped (with La³⁺, Ce³⁺, Nd³⁺, and Yb³⁺ ions) LiTmF₄ single crystals (Aminov et al. 1989). The absorption spectra of Tm³⁺ ions in LiTmF₄ (the ³H₆ \rightarrow ³F₂ transition, $T \approx 30$ K, σ -polarization) consists of three lines (fig. 21) due to electronic transitions between components of the ³H₆ and ³F₂ terms (fig. 22). The activation of the crystal by lanthanide ions gives rise to the distinctive changes of the Tm³⁺ absorption spectra. There appear satellites of the C-line (D, E lines in fig. 21b–d), which can be considered as a consequence of the splitting of the first excited Γ_{34} doublet of the Tm³⁺ ion (in fig. 22 the split states are shown by dashed lines). Satellite intensities are by an order of magnitude less than the intensity of the main spectrum line due to the low concentration (about 1%) of the impurity ions. The satellites move away from the C-line as the ionic radius of the impurity ion increases, and



Fig. 21. Optical absorption spectrum of the Tm³⁺ ions in the LiTmF₄ crystal without an impurity (a); in crystals containing 1% Nd³⁺ (b); 0.5% Ce³⁺ (c); 1% La³⁺ (d) (Aminov et al. 1989); temperature 30 K, σ polarization, ³H₆ \rightarrow ³F₂ transition.

for the LiTmF₄:Yb³⁺ crystal the splitting is not seen at all. The second component of the doublet (E-line), whose intensity is determined by the Boltzmann factor, is observed only in a LiTmF₄:Nd³⁺ crystal due to the better entry of Nd³⁺ ions into the matrix. The energy of the nearest excited level of the Tm³⁺ ion in the doped single crystals can be estimated from the position of the D-line: $\Delta' \approx 19.6$, 22.2, and 24.0 cm⁻¹ under implantation of the ions La³⁺, Ce³⁺, and Nd³⁺, respectively.

Thus, naturally there emerges the problem of a theoretical study of a detailed local crystal structure near impurity ions. Aminov et al. (1990b) have calculated local deformations in LiTmF₄ crystal with impurity lanthanide ions. The calculation of the local structure of a lattice with an isolated impurity ion (homovalent substitution) has been carried out within the framework of a "quasimolecular model of impurity centers" (Kristofel' 1974). The displacements $\delta(i)$ of the matrix ions from their positions in a regular lattice are assumed to be non-zero only within the "quasimolecule" including the defect site and 16 coordination shells nearest to it. The crystal bonding energy is expanded in power series up to the second order in $\delta(i)$ (harmonic approximation) and then minimized. At homovalent substitution the local deformation is determined entirely by forces on the nearest neighbours of an impurity ion (i.e., by the difference in the first derivatives of the potentials of the non-Coulomb interactions between impurity ions and their ligands on the one hand and host lanthanide ions and their ligands on the other).



Fig. 22. Energy levels of the Tm^{3+} ion in the LiTmF₄ crystal with the observed transition in the optical absorption spectrum marked.

The calculated values of displacements for ions of the first eight coordinational shells of impurity ions in the LiTmF₄ crystal are given in table 19. As expected, the displacements of the nearest neighbours of impurities are maximal and they correlate with the excess of the impurity ionic radii over that of Tm^{3+} ion [ionic radius of Tm^{3+} equals 0.99 Å; Lu^{3+} , 0.97 Å; Nd³⁺, 1.12 Å (Kaminskii 1975)]. It is seen that the ionic displacements do not decrease monotonously with the increase of the distance from an impurity ion.

The information obtained on the local structure of activated crystals has been used for estimates of energy spectrum changes for Tm³⁺ ions in different positions relative to an impurity ion. The energy change in a distorted lattice is described by the operator

$$\Delta \mathcal{H} \approx \sum_{pq} \Delta B_p^q O_p^q. \tag{196}$$

Some results of the calculations by means of an exchange charge theory, described in sect. 2, are given in table 20. The calculated energies E_1 of the first excited sublevels of the Tm³⁺ ions, closest to the impurity ions Nd³⁺, Ce³⁺, and La³⁺, are in satisfactory agreement with experimental data.

Taking proper account of static structure deformations and the corresponding change in the Stark spectrum upon implanting an impurity ion permits qualitative and, to a certain extent, quantitative explanation of all peculiarities observed by Mehran et al. (1977, 1982, 1983) in the temperature dependence of the EPR linewidth for impurity Gd^{3+} ions in lan-

NONMETALLIC LANTHANIDE COMPOUNDS

i	Ion	R_i	R_i (nm)	δ	(<i>i</i>)×10 ³ (nm)
				Nd ³⁺	Lu ³⁺
	F-	$(\frac{1}{2}-x, \frac{1}{2}-y, z),$	0.22215	(5.12, 4.56, 4.93)	(-1.11, -0.90, -1.08)
2	F-	$(\frac{1}{2}-x, -y, \frac{1}{4}-z),$	0.22745	(2.76, -4.01, 5.13)	(-0.60, 0.88, -1.08)
3	Li+	$(\frac{1}{2}, \frac{1}{2}, 0),$	0.36352	(1.85, 0.97, 0.60)	(-0.39, -0.19, -0.13)
ł	Tm ³⁺	$(0, \frac{1}{2}, \frac{1}{4}),$	0.36955	(0.67, 2.43, 1.63)	(-0.15, -0.52, -0.35)
i	Li+	$(\frac{1}{2}, 0, \frac{1}{4}),$	0.36955	(0.71, -0.21, 2.96)	(-0.15, 0.04, -0.62)
j –	F-	$(\frac{1}{2}-x,-\frac{1}{2}-y,-z),$	0.37034	(-2.09, 0.87, -1.04)	(0.47, -0.19, 0.23)
7	F-	$(\frac{1}{2} - y, x, \frac{1}{4} + z),$	0.41785	(-0.39, -0.52, 1.38)	(0.08, 0.12, -0.30)
;	F−	$(-\frac{1}{2}-x, \frac{1}{2}-y, z),$	0.44626	(-0.46, 1.13, -0.56)	(0.09, -0.24, 0.12)

Table 19 Displacements of ions in the LiTmF₄ crystal near impurity Nd^{3+} and Lu^{3+} ions^{a,b}

^a Aminov et al. (1990b).

^b Each of the eight coordinational shells considered consists of four similar ions. Coordinates for one of the four positions are given in units of lattice constants a, c. Parameters a, c, x, y, z, are given in the Introduction.

Table 20 Parameters of a quadrupolar component of a crystal field and energies of the Stark sublevels (in cm⁻¹) for Tm³⁺ ions in the LiTmF₄:Nd³⁺ crystal in different positions relative to an impurity ion, placed at the origin of coordinates ^a

R (Tm ³⁺)	ΔB_2^0	ΔB_2^1	ΔB_2^{-1}	ΔB_2^2	ΔB_2^{-2}	E_1	E_2	E_3
$(0, \frac{1}{2}, \frac{1}{4})$	-0.82	-25.3	18.5	30.9	34.4	20.6	43.5	62.5
(1,0,0)	4.45	-4.38	15.5	6.58	-15.5	28.0	32.0	58.5
$(1, \frac{1}{2}, \frac{1}{4})$	0.89	-7.70	-7.89	-6.00	-1.14	28.6	32.1	59.0
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	-1.49	15.8	19.7	-1.50	8.38	29.8	31.7	59.7
Regular ^b	0	0	0	0	0	30.5	30.5	59.4

^a Aminov et al. (1990b).

^b This row lists results of calculations for the regular $LiTmF_4$ lattice within the framework of the exchange charge model.

thanide zircons and in particular, the non-monotonous dependence of differences between linewidths of separate components of the EPR spectrum (Aminov and Kostetskii 1990).

3.6. Nuclear magnetic cooling

An intermediate character of the VV paramagnetism has specified their application in the magnetic cooling technique. The generation of ultralow temperatures by adiabatic demagnetization of common paramagnets has natural limitations due to the comparatively high $(>10^{-3} \text{ K})$ temperature of the magnetic ordering of electron spins (Wheatley 1975). To obtain temperatures below 10^{-3} K , adiabatic demagnetization of nuclear moments in metals is used, e.g., of ⁶³Cu and ⁶⁵Cu nuclei in metallic copper (Kurti et al. 1956).

In principle, the nuclear cooling does not differ from electron cooling, however, for its technical realization rigid initial conditions are needed, namely, in the former case the ratio H_0/T must be about 1000 times greater. Due to small values of the nuclear magnetic moments, it appears impossible to use the entropy (and therefore the cooling capacity) of the nuclear cooling stage completely. For example, an applied field of 80 kOe decreases the entropy of copper nuclei at a temperature of 20 mK by only 2.1%.

Thus, the idea of Al'tshuler (1966) to use VV paramagnets as nuclear refrigerants soon found its application in cryogenics (Andres and Bucher 1968, 1971). Enhancement of a magnetic field on nuclei of VV ions makes it possible to perform demagnetization in less rigid initial conditions, or to utilize the greater fraction of the sample's entropy in the same conditions. For example, the field of 80 kOe reduces the nuclear entropy of TmES already at 0.29 K (temperature of liquid ³He) by 2.1%. At T = 20 mK the entropy is removed almost completely.

In magnetic cooling experiments good thermal contact between the spin-system and the lattice is important. Therefore the most attention was directed towards the search of suitable intermetallic VV compounds (Andres 1978), in which the nuclear spin-lattice relaxation times are always much shorter, than in dielectrics, due to the presence of conduction electrons. Using the PrNi₅ compound, Andres and Darack (1977) reached a temperature of $0.8 \,\mathrm{mK}$ and reduced the ³He temperature to $1 \,\mathrm{mK}$. Later Folle et al. (1981) and Pobell (1982) obtained $0.19 \,\mathrm{mK}$ with the same compound.

One important fact should be mentioned, which to a great extent sustains further progress. Due to the conduction electrons in intermetallic compounds of lanthanides, the s-f exchange interaction is strong enough, and the temperatures of magnetic ordering of nuclear spins are high. For instance, in the above-mentioned $PrNi_5$ compound $T_C = 0.42 \text{ mK}$ (Kubota et al. 1983). At present it is advisable to use lanthanide intermetallic compounds as the first (preliminary) stage of a combined nuclear refrigerator, the traditional material (copper) serving as a second stage. In such a way Ishimoto et al. (1984) have reached a temperature of 27 μ K.

In dielectric VV paramagnets, nuclear spins are coupled to crystal lattice vibrations much more weakly than in intermetallic compounds; therefore it is difficult to cool the crystal lattice. However, very low temperatures of nuclear spin systems have been obtained: ¹⁶⁹Tm in TmVO₄, 0.1 mK; ¹⁶⁹Tm in TmPO₄, 0.4 mK (Suzuki et al. 1981); ¹⁶⁵Ho in HoVO₄, 1 mK (Suzuki et al. 1978).

Possibly, dielectrics will be used for deep cooling of ³He nuclei by direct transfer of the nuclear spin temperature across the crystal-liquid surface. Thus, when the nuclear spin-lattice relaxation rate of ¹⁶⁹Tm in TmES was investigated for different orientations of an applied field, a noticeable growth of that rate was found for the orientation, in which the resonance frequency of the thulium nucleus coincided with the frequency of the ³He nucleus (Egorov et al. 1984a). This bears evidence of a good contact between the two spin systems. Bleaney (1990) has suggested using adiabatic demagnetization of the VV paramagnets PrVO₄ and diluted $Y_xHo_{1-x}VO_4$ for reaching the temperatures 20– 200 µK. Vanadates are firm crystals and they may be pounded into very fine powder (with particle dimensions of $10-100\,\mu$), so the energy transfer to the surface by spin diffusion is accomplished within the acceptable time of 1-30 minutes.

3.7. Nuclear magnetic ordering

Nuclear magnetic cooling is closely connected with nuclear magnetic ordering. Nuclear antiferromagnetism was observed for the first time by Chapellier et al. (1969) on ¹⁹F nuclei in CaF₂. Since then nuclear ordering has been repeatedly investigated in different dielectric crystals. The comprehensive theory and experimental data are given in the monograph by Abragam and Goldman (1982).

For the usual nuclear spin systems in non-conducting diamagnetic crystals the ordering is due mainly to weak dipole-dipole interactions; consequently, the ordering temperature $T_{\rm C}$ is extremely low, of the order of microkelvins. To obtain such low temperatures by adiabatic demagnetization, it is necessary to polarize nuclei in high magnetic fields at initial temperatures of the order of several millikelvins. However, at such temperatures the spin-lattice relaxation is so slow, that it is necessary to use the method of dynamic nuclear polarization and, with this end in view, to insert a small number of paramagnetic centers. Clearly, these impurities produce a perturbing effect on a nuclear system in the ordered phase too.

In VV paramagnets the nuclear spin system can be polarized at more favourable ratios of the initial magnetic fields and temperatures, due to comparatively high values of the effective nuclear moments. For the same reason the ordering temperatures must be higher. Suzuki et al. (1978) have obtained the antiferromagnetic state of the ¹⁶⁵Ho nuclei in HoVO₄ with $T_N \approx 5 \text{ mK}$, in agreement with an estimate by Bleaney (1980). The nuclear entropy was reduced by direct magnetization at temperatures about 50 mK and subsequent demagnetization; as a result temperatures about 1 mK were reached. Nuclear ordering in HoVO₄ was investigated by methods of magnetic susceptibility (Suzuki et al. 1978), nuclear orientation (Allsop et al. 1981, Clark et al. 1987), neutron scattering (Suzuki et al. 1984), and nuclear quadrupole resonance of ⁵¹V (Bleaney et al. 1987). Besides, the antiferromagnetic phase nuclear spins of ¹⁶⁵Ho set up perpendicular to the *c*-axis, along the axes *a*; thus a domain structure may be manifested due to the presence of two equivalent axes *a*, *a'*.

The lifetime of the ordered state is finite due to the finite rate of the dipolar spin-lattice relaxation. For HoVO₄ this lifetime exceeds an hour (Clark et al. 1987), however it is significantly shorter (to about 200 s) in experiments with radiofrequency and modulating fields, and consequently the measurements become complicated (Bleaney et al. 1987).

In adiabatic demagnetization experiments, Suzuki et al. (1983) observed antiferromagnetic ordering of the enhanced nuclear spin system of Ho in $Cs_2NaHoCl_6$ with the ground nonmagnetic doublet at 1.5 mK. Murao (1988) considered the coupled equations of motion of the electron and nuclear magnetic moments in this crystal with reference to the antiferromagnetic resonance experiments. Some other examples of the electronnuclear ordering in lanthanide dielectric compounds are presented in the next section.

Abragam and Bleaney (1983) discussed the possibility of obtaining the ordered nuclear states in TmPO₄ and LiTmF₄ crystals, similar to vanadates. The expected ordering temperature in these compounds is less than 10 μ K due to the lower values of the γ_{\perp} -factor and nuclear spin. To obtain such low temperatures it is necessary to apply methods used for conventional nuclear magnets.

4. Ferro- and antiferromagnets

4.1. Paramagnetic susceptibility

Systems with a magnetic ground state at low temperatures undergo transitions into magnetically ordered phases. The ordering in lanthanide dielectrics may be regarded as an alignment of the point magnetic dipoles; as a result a quasi static magnetic field which may be simply calculated is established in a sample. A high degree of polarization (alignment) can also be achieved by applying an external magnetic field.

Some definitions used in the theory of magnets are appropriate at this point. An elementary cell is assumed to contain *n* magnetically equivalent ions. When the low-temperature range is considered, only the ground magnetic doublet in an ion spectrum can be accounted for. The magnetization of a crystal in a paramagnetic phase equals $\chi' H_{loc}$ in accordance with eqs. (106) and (107) and the local magnetic field can be written as

$$H_{\rm loc} = H_0 + H_{\rm ex} + H_{\rm d} + H_{\rm L} + H_{\rm D}.$$
 (197)

According to eqs. (72) and (76), we have singled out an exchange field

$$\boldsymbol{H}_{\mathrm{ex}} = \boldsymbol{\Lambda}_{\mathrm{ex}} \boldsymbol{M},\tag{198}$$

which is defined through the dimensionless constants

$$\Lambda_{\rm ex,a\beta} = -\frac{\upsilon}{n(g_{\rm J}\mu_{\rm B})^2} \sum_{\lambda'} A_{a\beta}(\lambda,\lambda'), \tag{199}$$

a field $H_d = A_d M$ of point dipoles within a sphere centered on one of the magnetic sublattice sites, whose radius is much greater than the interionic distance; the Lorentz field $H_L = (4\pi/3)M$, corresponding to the field of dipoles outside the chosen sphere in the continuum approximation, and demagnetizing field H_D . The latter is inhomogeneous in the general case and depends on the sample shape; for ellipsoidal samples $H_D = -DM$, where $D_{\alpha\beta}$ are demagnetizing factors. The tensor of dipolar field constants can be found either by the direct calculation of lattice sums within a sphere (cf. eq. 153), or by the use of the Ewald method (see eq. 45):

$$\Lambda_{\rm d,\alpha\beta} = \frac{\upsilon}{n} \sum_{\lambda'} \left[Q_{\alpha\beta}(\lambda\lambda') - \frac{4\pi}{3\upsilon} \delta_{\alpha\beta} \right].$$
(200)

According to eq. (197) the measured paramagnetic susceptibility takes the form

$$\boldsymbol{\chi}^{(T)} = \left[1 - \boldsymbol{\chi}'(\boldsymbol{\Lambda}_{\text{ex}} + \boldsymbol{\Lambda}_{\text{d}} + \frac{4\pi}{3}\boldsymbol{1} - \boldsymbol{D})\right]^{-1}\boldsymbol{\chi}'.$$
(201)

In particular, if the effective spin Hamiltonian of ions looks like eq. (119) (a Kramers or non-Kramers doublet with $g_{\perp}=0$ in an axially symmetric crystal field), then neglecting the VV magnetization, we have

$$\chi'_{\parallel} = \frac{ng_{\parallel}^{2}\mu_{\rm B}^{2}}{4\nu k_{\rm B}T},\tag{202}$$

so the measured susceptibility for a spherical sample $[D = (4\pi/3)1]$ equals

$$\chi_{\parallel}^{(T)} = \frac{C_{\parallel}}{T - \Theta_{\parallel}},\tag{203}$$

where $C_{\parallel} = ng_{\parallel}^2 \mu_{\rm B}^2 / 4vk_{\rm B}$ is the Curie constant, and $\Theta_{\parallel} = C_{\parallel} (\Lambda_{\rm ex\parallel} + \Lambda_{\rm d\parallel})$ is the Curie–Weiss temperature.

In crystals with a positive Curie–Weiss temperature long-range order (ferromagnetic state) occurs at lower temperature, with the transition point $T_{\rm C} = C_{\parallel}(\Lambda_{\rm ex\parallel} + \Lambda_{\rm d\parallel} + 4\pi/3)$, for which the susceptibility of a sample with zero demagnetizing factor diverges. Thus, for dipolar ferromagnets the paramagnetic susceptibility equals

$$\chi_{\parallel}^{(T)} = \frac{C_{\parallel}}{T - T_{\rm C} + C_{\parallel} D_{\parallel}},\tag{204}$$

and for real specimens it remains finite at the transition point. The magnetic susceptibility of antiferromagnets is described by Abragam and Goldman (1982).

The dipolar magnetization in a finite ferromagnetically ordered specimen splits into the long needle-like domains with zero demagnetizing factors, the needles being parallel to the easy magnetization axis. The energy of a sample per unit volume equals $(D_{\parallel}M^2/2)$ in the demagnetizing field H_D , so the formation of the domains with $D_{\parallel} = 0$ is of advantage. In Ising ferromagnets the direction of magnetic moments at the domain walls is abruptly reversed. Following Kittel (1949), we can estimate the domain width d for which the sum of the domain wall energy ($\sim aMH_i$, where a is the lattice constant and $H_i = \Lambda M$ is the internal magnetic field with $\Lambda = \Lambda_{ex} + \Lambda_d + 4\pi/3$) and the surface energy ($\sim M^2 d$) of

a sample is minimal. The energy per unit volume of a domain with the length l_z (the sample dimension in the M direction) equals $M^2[(a\Lambda/d) + (d/l_z)]$, and the condition of its minimum yields $d \approx \sqrt{a\Lambda l_z}$. The estimation $d \approx 4 \times 10^{-4}$ cm for samples with dimension $l_z \approx 1$ cm and $\Lambda \approx 4$, $a \approx 5$ Å, agrees with the results of optical investigations by Battison et al. (1975) of the LiHoF₄ samples ($d = 5 \times 10^{-4}$ cm). A similar estimation (by an order of magnitude) of the domain width in DyES was obtained by Cooke et al. (1968). The domain width is insensitive to the form of the domains and to the curvature of the specimen surface, provided they are long in the M direction.

An interesting problem in the physics of the dipolar ferromagnets with the uniaxial anisotropy is the evolution of the domain structure in the thin slabs cut perpendicular to the easy axis. The short-range attractive interactions lead to the local alignment of magnetic dipoles and the long-range repulsive forces lead to a competitive antialignment. At low temperatures in the zero external field the slab spontaneously orders into a structure of stripe domains. If an applied magnetic field exceeds the critical value depending on the slab thickness, a first order transition takes place to the bubble phase which disappears in the fields $H_0 > H_{0c}$. Such modulated phases with a spontaneous spatial variation of the magnetization were directly detected by a Faraday technique in thin LiHoF₄ films by Pommier et al. (1988).

Since the transverse dimensions of the domains are of the order of infra-red radiation wavelengths, their formation may be followed by the wave-guide effect, which has been observed by Kupchikov et al. (1987) in the LiTbF₄ crystal. Another striking optical property of the dipolar ferromagnets is the domain diffraction produced in the ferromagnetic state (see Griffin and Litster (1979) and references therein). In each domain the population difference in the ground states produces a large circular birefringence. In the down domains $n_{\rm RCP} \gg n_{\rm LCP}$, while in the up domains $n_{\rm LCP} \gg n_{\rm RCP}$, where $n_{\rm RCP}$ and $n_{\rm LCP}$ are the indices of refraction for the right and left circularly polarized light, respectively. As a result, the domains form a phase grating, the periodicity of which is determined by the spacing and shape of the domains, and the depth of which is determined by the magnitude of $|n_{RCP} - n_{LCP}|$. In the paramagnetic phase at zero external field, the circularly polarized light, propagating parallel to the symmetry axis, passes through the sample essentially unaffected. In the ordered phase this beam encounters a phase grating and part of the transmitted intensity is diffracted into outer lobes. In the presence of H_0 the phase grating changes. At constant temperature $T < T_{\rm C}$ the application of an external magnetic field $H_0 || M$ modifies the fraction of domains that are parallel and antiparallel to the field direction. The parallel domains grow in number at the expense of the antiparallel domains. However, in each domain the magnetization M_{sp} remains constant, so does the internal field, and $H_0 + D_{\parallel}M = 0$, where M is the sample magnetization. Although a periodic diffraction pattern has not as yet been observed (the domains are unlikely to consist of uniformly spaced cylinders or plates), the technique of locating the onset of domain diffraction is used to map out the ferromagnetic-paramagnetic phase boundary and to measure the spontaneous magnetization $M_{\rm sp} = H_{\rm 0c}/D_{\parallel}$, where $H_{\rm 0c}$ is the intensity of the external field at which the domain pattern (and the beam attenuation) disappears. The plateau in the dcparallel susceptibility at $T < T_{\rm C}$, when $\chi_{\parallel}^{(T)} = 1/D_{\parallel}$, is a characteristic feature of dipolar ferromagnets. The ac-susceptibility may have a maximum at $T_{\rm C}$ due to the finite velocity of the domain wall movement.

The dynamic susceptibility of some uniaxial lanthanide ferromagnets both in monoand multidomain regions of an external magnetic field was studied at frequencies from several Hz to hundreds of MHz (DyES, Cooke et al. 1968; R(OH)₃, Schlachetzki and Eckert 1972; TbAsO₄, Muller et al. 1983; LiTbF₄ and LiTb_{0.9}Y_{0.1}F₄, Kotzler et al. 1984; GdCl₃, Grahl and Kotzler 1989). In particular, it was found that in the multidomain state $(T \rightarrow 0, H_0 \rightarrow 0)$ the domain relaxation rate was fast compared to the rate of the spinlattice relaxation (1 Hz) and small compared to the spin–spin relaxation (40 MHz) in the LiTbF₄ crystal. The Y³⁺ impurities reduce the domain relaxation rate corresponding to larger barriers.

Internal magnetic fields with complex configuration and their fluctuations determine distinctive features of NMR of the magnetically concentrated systems in question, of which we note the following:

- the observation of stationary NMR by scanning the magnetic field or frequency turns out to be hindered because of the extremely high nonresonant absorption of radiofrequency field energy by the electron spin system;
- (2) pulsed NMR (spin echo) is observed only in conditions of high electron spin polarization, that is, as a rule, at temperatures below 1 K;
- (3) nuclei are affected by strong internal (molecular) fields, quantization axes of nuclear spins in different crystallographic positions are oriented differently and in general do not coincide with the direction of an external magnetic field;
- (4) NMR frequencies of nuclei in different crystallographic positions strongly differ, therefore the energy exchange between systems of different nuclear spins is hampered.

Here the susceptibility and internal magnetic fields in TbES and DyES are considered in greater detail. The energy levels of Tb^{3+} ions in TbES are given in table 5. At liquid helium temperatures and below magnetic properties of the Tb^{3+} ion are completely determined by the two lowest singlets

$$\psi(\varepsilon_1 = 0, \Gamma_1) = 0.7058(|6\rangle + |-6\rangle) + 0.0600 |0\rangle, \psi(\varepsilon_2 = 0.4 \text{ cm}^{-1}, \Gamma_2) = 0.7071(|-6\rangle - |6\rangle),$$

forming a quasidoublet. The splitting of these states in a magnetic field is determined by the spin Hamiltonian (123) with the parameters given in table 11. The wave functions of the quasidoublet in a magnetic field H_z parallel to the crystal *c*-axis can be put down fairly well as follows:

$$|\psi_1\rangle = (1 + \kappa^2)^{-1/2} (|6\rangle + \kappa |-6\rangle), \qquad |\psi_2\rangle = (1 + \kappa^2)^{-1/2} (-\kappa |6\rangle + |-6\rangle),$$
(205)

where

$$\kappa = \frac{(\delta - g_{\parallel} \mu_{\rm B} H_z)}{\delta_0}, \qquad \delta = (\delta_0^2 + g_{\parallel}^2 \mu_{\rm B}^2 H_z^2)^{1/2}.$$
(206)

Atom	Σ_x	Σ_y	Σ_z
R	0.000	0.000	0.742
H5A1	-2.878	-3.627	-0.405
H5A2	4.582	-0.680	-0.405
H5A3	-1.704	4.311	-0.405
H5B1	-0.610	-4.774	3.762
H5B2	4.439	1.859	3.762
H5B3	-3.833	2.915	3.762
H41	-1.345	1.653	-2.202
H42	-0.761	-1.993	-2.202
H43	2.104	0.338	-2.202
H21	0.566	0.253	-1.159
H22	-0.502	0.363	-1.159
H23	-0.063	-0.616	-1.159
H1A1	0.000	0.000	-0.763
H1A2	0.000	0.000	-0.763
H1A3	0.000	0.000	-0.763
H1B1	0.013	0.032	-0.740
H1B2	-0.034	-0.005	-0.740
H1B3	0.022	-0.027	-0.740

 Table 21

 Lattice sums over lanthanide ions (eq. 208), determining components of the molecular field at all protons of a RES molecule and at the R³⁺ ion^a

^a The x-axis is directed along the crystallographic a-axis, summation is carried out over the ions inside a sphere with a diameter of 35 Å, the results are given in 10^{22} cm⁻³; the lattice parameters of the YES crystal are used.

At very low temperatures $(k_{\rm B}T \ll \delta)$ all Tb³⁺ ions in a crystal are in the lower quasidoublet sublevel and their magnetic moment components are

$$\mu_x = \mu_y = 0, \qquad \mu_z = \frac{1}{2}g_{\parallel}^2 \mu_{\rm B}^2 H_z (\delta_0^2 + g_{\parallel}^2 \mu_{\rm B}^2 H_z^2)^{-1/2}; \tag{207}$$

in the absence of a magnetic field one has $\mu_z = 0$, while in the high-field limit $\mu_z^{\text{max}} = 8.91 \mu_{\text{B}}$.

The lowest energy level of the Dy^{3+} ion (${}^{6}H_{15/2}$) in ethylsulfate is an ordinary Kramers doublet (see table 5) with

$$\psi(\Gamma_{9,10}) = \pm 0.06 \left| \pm \frac{15}{2} \right\rangle \pm 0.27 \left| \pm \frac{3}{2} \right\rangle \pm 0.96 \left| \pm \frac{9}{2} \right\rangle,$$

which is not split in the first order on H_0 by the magnetic field perpendicular to the *c*-axis ($g_{\perp}=0$). The splitting of the doublet in a magnetic field parallel to the *c*-axis is determined by factor $g_{\parallel}=10.8$ (Abragam and Bleaney 1970, Powell and Orbach 1961) and the corresponding magnetic moment of the Dy³⁺ ion in the ground state equals $\mu_z = 5.4 \mu_{\rm B}$.

A field operating on a spin inside a magnetized sample of a spherical shape reduces to a sum of an applied and dipolar field. In the simplest model of a molecular field its source can be presented as point dipoles, so components of the field on a nucleus are determined by lattice sums over lanthanide ions:

$$H_{d\alpha} = \mu_z \Sigma_{\alpha},$$

$$\Sigma_x = 3 \sum_j x_j z_j r_j^{-5}, \qquad \Sigma_y = 3 \sum_j x_j z_j r_j^{-5}, \qquad \Sigma_z = \sum_j (3z_j^2 - r_j^2) r_j^{-5}, \qquad (208)$$

where r_j is the radius-vector of the *j*-th ion related to the point in which the field is calculated. A qualitative picture of molecular fields within the TbES and DyES crystals is shown in fig. 2. Table 21 contains lattice sums corresponding to all the protons of an ethylsulfate molecule. The sum Σ_z^R determining the molecular field on a lanthanide ion is also given there.

4.2. Magnetic ordering and critical phenomena

Among the different two-particle interactions, the dipole-dipole interaction may be the most important in the magnetic ordering of lanthanide dielectrics, especially in compounds of the heavy trivalent lanthanide ions (Tb, Dy, Ho, Er, Tm) with a large angular moment of the ground multiplet. The absence of unknown parameters in the Hamiltonian of dipolar interactions makes it possible to analyze the problem with no difficulties in estimating the corresponding effects, but the long-range and competitive character of the dipolar forces (their signs may be both positive and negative depending on the orientation of the vector that connects the two dipoles) manifests itself in some qualitative peculiarities of the magnetic ordering. First of all we encounter the problem of finding the magnetic structure of the ordered phase and estimating its critical temperature. The stable magnetic structure may in principle be found by comparing the energies of different magnetic moment configurations in the lattice at zero temperature. In some cases this task may be handled analytically with the method of Luttinger and Tisza (1946). In this method the spins are considered as classical quantities and their total length is considered fixed. Let us assume that the magnetic structure corresponds to the space group irreducible representation with the wave vector in the Brillouin zone center or from the zone boundary, i.e. it has the same periodicity or twice that of the Bravais lattice. In the case of n = 1, 2 equivalent dipoles per unit cell the problem involves finding the minimum of the interaction energy (per spin)

$$E = -\frac{1}{16n} \sum_{ij\alpha\beta} \mu_{i\alpha} Q_{\alpha\beta}(i,j) \mu_{j\beta}, \qquad (209)$$

represented by the 24*n*-dimensional quadratic form in directional cosines of the dipoles μ_i from the 8*n* sublattices with the unit cell dimensions $2a \times 2b \times 2c$ (no demagnetizing fields arise from infinity and the matrix Q is defined in eq. 45). The minimum of

eq. (209) is related to the transition temperature: $E_{\min} = -0.5 k_B T_C$ for $S = \frac{1}{2}$ (Felsteiner and Friedman 1973) and the corresponding eigenvector determines the dipole arrangement. The additional constraints on the individual dipole lengths for the ferromagnetic, purely antiferromagnetic (Néel) and layered antiferromagnetic structures are fulfilled automatically due to the translational symmetry of the lattice (Felsteiner and Misra 1973, Niemeijer and Meijer 1974). In most cases the results of calculations performed for lanthanide ethylsulfates, garnets, hydrated chlorides, hydroxides, double fluorides and lanthanide high- T_c superconducting cuprates agree with the experimental data (Capel 1965, Felsteiner 1970, Lagendijk et al. 1972, Misra and Felsteiner 1977, 1992, Anders and Volotskii 1992).

The calculation of the ground-state energy of the classical dipole system does not provide an answer the question about the stability of the corresponding ordered dipole array. The magnetic moments of individual particles do not commute with the Hamiltonian of the dipole-dipole interaction, and quantum fluctuations may essentially affect the results of the classical approximation even at zero temperature. The magnetic structure is stable only in the case of positive excitation energies of the system. It should also be noted that for magnetic ions in the cubic crystal field with isotropic g-factors and in the case of the easy plane for magnetization as well, the magnetic structure with the minimum of energy may appear degenerate. In the real compounds the electron-deformation interaction (spontaneous magnetostriction) and the higher order effects of the dipole-dipole interaction involving the excited sublevels of the ground multiplet can induce the anisotropy of magnetization. However, the quantum corrections, in particular the dependence on the dipole directions of the zero-point energy of the quasiparticle (magnon) excitations, may be of the primary importance. The average spin values are reduced at magnon excitations and this reduction, depending on the lattice structure, g-factors and temperature, remains finite at T=0. Until recently the quantum-mechanical conditions of stability, anisotropy and average magnetization of ferromagnetic and two-sublattice antiferromagnetic arrays of point dipoles in primitive cubic lattices were only examined numerically by Cohen and Keffer (1955) and Corruccini and White (1993) in the spin-wave approximation with the Holstein and Primakoff (1940) transformation. The classical results indicating the lowest energy of an antiferromagnetic array for a simple cubic lattice and of ferromagnetic arrays for the body-centered and the face-centered cubic lattices were confirmed, and it was shown that the zero-point corrections to the classical energy (decreasing with the value of spin S) may have the same order of magnitude as the energy differences between different dipole arrangements. The ferromagnetic ordering in the series of $Cs_2NaR(NO_2)_6$ crystals with the face-centered cubic lanthanide sublattice investigated by Roser and Corruccini (1990) is consistent with the theoretical predictions.

The data available in the literature on magnetic ordering temperatures in the insulating crystals containing trivalent lanthanide ions are presented in table 22. Magnetic ordering was also found in Dy₂TiO₅ ($T_{\rm N}$ = 1.55 K, Cashion et al. 1968), Dy₂GeO₅ ($T_{\rm N}$ = 2.5 K, Wanklyn 1973), Er₂GeO₅ ($T_{\rm N}$ = 1.25 K, Wanklyn 1973), BaEr₂F₈ ($T_{\rm N}$ = 1.73 K, Bleaney et al. 1995), CsGd(MoO₄)₂ ($T_{\rm N}$ = 0.448 K, Anders et al. 1995). Here we shall only briefly

comment on the possible overall classifications and on some peculiarities of the magnetic properties of different compounds.

First of all we have divided the lanthanide group into two sets: Kramers and non-Kramers ions. The column of Ce compounds is almost empty (magnetic ordering in these compounds occurs at very low temperatures and the mixed-valent behaviour of Ce ions may also prevent ordering). The numerical values of the ordering temperature correlate mainly with the volume per spin V_S . For crystals with $V_S > 200 \text{ Å}^3$ such as elpasolites ($V_S \approx 1000 \text{ Å}^3$), hydrated chlorides ($V_S \approx 240 \text{ Å}^3$) and sulfates ($V_S \approx 200 \text{ Å}^3$), ethylsulfates ($V_S \approx 600 \text{ Å}^3$), bromates ($V_S \approx 400 \text{ Å}^3$), and trifluoromethane sulfonates ($V_S \approx 610 \text{ Å}^3$) the interaction between the magnetic ions is predominantly or purely dipolar (with possible contributions from the exchange through the long-wave phonons), and the long-range magnetic ordering is observed only at ultralow temperatures. In crystals with the high density of lanthanide ions exchange interactions between the nearest neighbours are comparable in magnitude or even stronger than the magnetic dipolar interactions, and the ordering temperatures lie in the liquid helium range.

Estimations of the interionic interactions, using the magnitude of a volume per magnetic ion, can be made only superficially. In fact, the arrangement of magnetic ions in the real lattice may be highly anisotropic. Depending on lattice constants the lanthanide ions can form chains with the interchain intervals being essentially larger than the interionic distances between the nearest neighbours in the chain or they can form planes divided by large intervals (quasi two-dimensional structure) as in the high- T_c R–Ba–Cu–O superconductors.

There are some peculiarities of magnetic ordering in the non-Kramers systems, where magnetization is extremely anisotropic and its single direction is determined by the crystal field (see eq. 123). The cooperative phenomena in these compounds may be well approximated by some kinds of Ising systems, in particular, by the Ising model in the transverse field in the case of a quasidoublet ground state. However, the problems of singlet magnetism and of the competition between magnetic and structural orderings demand special examination. The ordering of the 4f-shell multipoles interacting with each other through the static and dynamic lattice deformations (the cooperative Jahn-Teller effect) involves the lowering of crystal symmetry and corresponding changes in the lanthanide subsystem energy (Harley 1987). The Jahn-Teller phase transitions were observed in many compounds of the lanthanide non-Kramers and Kramers ions having sublevels with small excitation energies in their spectra and the corresponding critical temperatures $T_{\rm D}$ are presented in table 22. If the Zeeman energy of the ion with a non-Kramers ground doublet does not commute with the energy of the interaction with the spontaneous deformation an external magnetic field suppresses the structural phase transition. In this case the magnetic ordering does not take place at temperatures below $T_{\rm D}$. Thulium vanadate presents an example of such a system.

The enhanced nuclear magnetism of the non-Kramers ions considered in detail in the preceding section can play a crucial role in establishing the long-range magnetic order in an electronic singlet ground state system. Let us consider the simplest example of such

			Temperatu	res (K) of r	nagnetic a	nd structu	ral orderii	ıg in lanth	anide insula	tors				
Compound (Bravie Jattice)	Space group	R-site	4f ¹ , C_3+	4f ³ , Nd ³⁺		4f ⁵ , c _{m3+}	4f ⁷ , Gd ³⁺	4f ⁹ , 13+	4f.1,	4f ¹³ , vr, ³⁺	4f ² ,	4f ⁸ , Tr, ³⁺	4f	°.≓	4f ¹² , T ³⁺
(Diavais lauro)		symme	$\frac{1}{T_0^a}$ Rf	Toa	Rf	T ₀ ^a Rf	T_0^{a} Rf	T_0^{a} Rf	T_0^{a} R	$\frac{10}{f}$ $\frac{10}{T_0^a}$ Rf	T_0^{a} Rf	T ₀ ^a R	$\frac{1}{f}$	Rf	T_0^{a} Rf
R2O3 (Cv)	$Ia\bar{3} T_h^7$	C2 C3i					1.35 ^b 1	1.2 2	3.36 3	2.30 4		2.42 5	1.2	0	
R3Al5O12 (Cv)	IaĨd Oh	D_2					2.54 7	2.54 8				1.35 9	0.86	10	
R ₃ Ga ₅ O ₁₂ (Cv)	Ia3d O _h	D_2		0.516	11	0.918 11		0.373 12	0.789 11	0.054 12		0.24 13	0.15	13	
RAIO ₃ (0)	Pmma D ¹⁶ 2h	రి					3.87 14	3.53 15	0.60 16			3.955 15	0.16	17	
RCoO ₃ (O)	Pnma D ¹⁶ 2h	౮					2.9 18	3.6 18				3.3 18	2.4	18	
$R_2Ti_2O_7$ (Cf)	$Fd\bar{3}m O_h^7$	D_{3d}						1.35 19	1.25 20	0.214 20			1.40	19	
R2Ge2O7 (Q)	$P4_12_22 D_4^4$	Ċ						2.15 21	1.15 21			2.05 21	1.45	21	
$R_2Zr_2O_7$ (Cf)	Fd3̃m O _h	D_{3d}		0.37	20										
R ₂ Sn ₂ O ₇ (Cf)	$Fd3m O_h^7$	D_{3d}		0.91	20										
R2GaSbO7 (Cf)	Fd3m O _h	D_{3d}		1.158	20										
RNbO4 (Mc)	$12/c C_2^3$	c_2					1.67 19	1.52 19				1.82 19			
R_2O_2S (H)	P3m1 D3d	c_{3v}					5.7 22	5.13 22		2.575 23		6.0 22	2.25	22	
R ₂ O ₂ Se (H)	P3ml D _{3d}	C_{3v}					6.7 24	8.5 24		1.5 24		7.0 24	4.0	24	
R2O2Te (Qv)	$14/mmm D_{4h}^{17}$	$\mathrm{D}_{4\mathrm{h}}$						10.2 24							
R2O2SO4 (0)	Pnma D ¹⁶ 2h	c ⁱ					4.51 25	8.13 26	1.50 26			3.92 26	3.59	26	1.76 26
ROCI (Q)	$P4/nmm D_{4h}^{7}$	C_{4v}						9.0 27				4.0 27			
RPO4 (Qv)	141/amd D ¹⁹ 4h	D_{2d}						3.4 28	3.0 29	_		2.28 30	1.39	31	
												2.13 ^c 30			
RVO4 (Qv)	I4 ₁ /amd D ¹⁹ 4h	D_{2d}					2.495 32	14.0 ^d 33, 34	< 0.4 29	0.093 35		33.9 ^d 36	0.004	5 37	2.14 ^d 38
	D_{28}^{28}	ں۔ ت						3.05 33.							
	17	ĩ						34							
	D_{2h}^{24}	\mathbf{D}_2										0.61 36			
													continu	uo pəi	next page

Table 22 s (K) of magnetic and structural ordering in lanthanide

410

L.K. AMINOV et al.

						ĺ							
Compound (Bravais lattice)	Space group	R-site symm.	4f ¹ , Ce ³⁺	4f ³ , Nd ³⁺	4f ⁵ , Sm ³⁺	4f ⁷ , Gd ³⁺	$4f^9$, Dy^{3+}	4f ¹¹ , Er ³⁺	4f ¹³ , Yb ³⁺	4f ² , Pr ³⁺	4f ⁸ , Tb ³⁺	4f ¹⁰ , Ho ³⁺	4f ¹² , Tm ³⁺
			To ^a Rf	To ^a Rf	To ^a Rf	T_0^{a} Rf	T_{o}^{a} Rf	To ^a Rf	T_0^a Rf	To ^a Rf	To ^a Rf	To ^a Rf	T_0^a Rf
RAsO4 (Qv)	14 ₁ / <i>a</i> md D ¹⁹ _{4h}	D_{2d}				1.262 39	11.2 ^d 34, 40		0.30 41		28.0 ^d 42	0.56 43	6.13 ^d 44
	$\mathrm{D}^{28}_{2\mathrm{h}}$	C_{2v}					2.51 34, 40						
	D_{2h}^{24}	D_2									1.48 42		
LiRF4 (Qv)	I41/a C ⁶	S4					0.605 45	0.38 46			2.885 ^b 47	1.538 ^b 48	
BaR ₂ F ₈ (Mc)	$C2/m C_{2h}^3$	C_2										1.76 49	
RF ₃ (O)	Pnma D ¹⁶ 2h	ڻ				1.15 ^b 1					3.95° 50	0.53 ^c 51	
R(OH) ₃ (H)	P6 ₃ /m C ² _{6h}	C_{3h}		0.265 52		0.94 53	3.48 ^b 54			1.21 ^d 55	3.71 ^b 54	2.54 ^b 54	
RCl ₃ (H)	P63/m C ² 6h	C_{3h}	0.115 56	0.5 57		2.2 ^b 58				0.41 ^d 59			
RBr ₃ (H)	P6 ₃ /m C ² _{6h}	C_{3h}								0.37 ^d 59			
R(C2H5SO4)3: 9H2O (H)	P63/m C ² _{6h}	C_{3h}				0.030 60	0.127 ^b 61				0.24 ^b 62	0.215 63	
R(CF ₃ SO ₃) ₃ : 9H ₂ O (H)	P63/m C ² _{6h}	C_{3h}					0.111 ^b 64			0.31 65	0.24 ^b 64	0.224 ^b 64	
R(BrO ₃) ₃ :9H ₂ O (Oc)	C_{2v}^{12} (P6 ₃ /mmc) ^e (D ⁴ _{6h})	(D _{3h}) ^e					0.161 ^b 66				0.125 ⁶ 66		
RCl ₃ :6H ₂ O (M)	P2/m C ¹ _{2h}	c2				0.20 ^b 1	0.289 ^b 67	0.353 ^b 67					
R(NO ₃) ₃ :6H ₂ O (M)	PĪ C¦	cı				0.95 ^b 1							
R ₂ (SO ₄) ₃ :8H ₂ O (Mc)	$C2/c C_{2h}^{6}$	cı				0.182 ^b 1					0.15 ^c 68		0.285°69
KR(MoO4)2 (O)	$Pbcn D_{2h}^{14}$	C_2					14.3 ^d 70 1.1 ^c 71	0.9 72					
											c	continued o	n next page

Table 22, continued

411

							Table 2	22, con	tinued						
Compound (Bravais lattice)	Space group	R-site symm.	$\begin{array}{c} 4f^{l},\\ Ce^{3+}\\ T_{0}^{a} Rf \end{array}$	$4f^{3}$ Nd^{3} T_{0}^{3}	Rf	$\frac{4f^5}{Sm^{3+}}$	tr 10	tf ⁷ , jd ³⁺ a Rf	$4f^9,$ Dy^{3+} $T_0^a Rf$	$4f^{11},$ Er^{3+} $T_0^a Rf$	$\frac{4f^{13}}{Yb^{3+}},$ $\frac{Yb^{3+}}{T_0^{8} Rf}$	4f ² , Pr ³⁺ r _o ^a Rf	$\frac{4f^8}{Tb^{3+}},$ $\frac{Tb^{3+}}{T_0^a Rf}$	$\begin{array}{c} 4f^{10},\\ Ho^{3+}\\ T_0{}^a Rf \end{array}$	$4f^{12},$ Tm^{3+} $T_0^{a} Rf$
RbR(MoO4)2 (O)	Pbcn D_{2h}^{14}	50							19.0 ^d 73						
Csr(MoU4)2 (U) Cs2NaRCI6 (Cf)	F <i>ulo</i> C _{2h} F m 3m O _h	ర్					0.0	35 ^b 75	0.021 ^b 75	0.050 ^b 75				0.15 ^d 76 0.0048 77	
Cs ₂ NaRF ₆ (Cf)	Fm3m O _h	ő												0.393 ^d 78	
Cs ₂ NaR(NO ₂) ₆ (Cf)	Fm3 T_h^3	$\mathbf{T}_{\mathbf{h}}$		0.006	6L9		0.0	45 ^b 79	0.060 ^b 79	0.040 ^b 79					
RPO4(MoO ₃) ₁₂ : 30H ₂ O (Cf)	Fd3̃m O _h	T _d					0.0	21 80	0.030 80	0.017 80					
R2CuO4 (Qv)	$I4/mmm D_{4h}^{17}$	D_{4h}		1.5	81	5.95 8	2 6.5	82							
RBa ₂ Cu ₃ O ₆ (Q)	P4/mmm D ¹ _{4h}	D_{4h}		1.5	83						7	.5 84			
RBa ₂ Cu ₃ O ₇ (O)	P/mmm D ¹ _{2h}	$\mathbf{D}_{2\mathrm{h}}$		0.551	85	0.60 8	5 2.2	85	0.92 86	0.618 86	0.35 87 17	9 88		0.17 89	
RBa2Cu4O8 (Oc)	Ammm D ¹⁹	$\mathrm{D}_{2\mathrm{h}}$							1.1 91	0.49 90				0.100 91	
R ₂ Ba4Cu7O ₁₅	Ammin D_{2h}^{19}	$\mathrm{D}_{2\mathrm{h}}$							1.25 92						
RBa ₂ Cu ₂ NbO ₈ (Qv)	I4/mcm D ¹⁸ 4h	D_{4h}		1.69	93						12	.7 93			
4f ¹ : Pr ⁴⁺ , 4f ⁷ : Tl	P4+ ₽														
RO2 (Cf)	Fm3m Oh	ч ^ч о	4 94				ŝ	94							
RBaO ₃ ^f			11.7 95				34	95							

412

L.K. AMINOV et al.

continued on next page

^a Antiferromagnetic ordering, unless indicated otherwise. ^b Ferromagnetic ordering.		
^b Ferromagnetic ordering.	^d Jahn–Te	iller ferroelastics.
	^e This sy	nmetry corresponds to average BrO_3^{-} anion positions.
^c Canted ferromagnets.	f Symme	ries differ for BaPrO ₃ [Phum (D_{2h}^{16}, C_s)] and BaTbO ₃ [R $3c$ (D_{3d}^{6}, D_3)].
References		
(1) Katila et al. (1970) (3:	33) Will and Schäfer (1971)	(65) Petasis et al. (1993)
(2) Bonrath et al. (1966b) (34	34) Kasten (1980)	(66) Simizu et al. (1986)
(3) Tang et al. (1992) (3:	35) Radhakrishna et al. (1981)	(67) Lagendijk et al. (1972)
(4) Henry (1955) (3)	36) Gehring et al. (1976a)	(68) Simizu and Friedberg (1981)
(5) MacChesney et al. (1966) (3)	37) Suzuki et al. (1984)	(69) Katila et al. (1972)
(6) Bonrath et al. (1966a) (3)	38) Gehring and Gehring (1975)	(70) Cooke et al. (1976)
(7) Guttmann (1975) (3)	39) Colwell et al. (1971)	(71) Zvyagin et al. (1973)
(8) Kolmakova et al. (1990) (4)	40) Kahle et al. (1971)	(72) Pshisukha et al. (1976)
(9) Belov and Sokolov (1977) (4	41) Hodges et al. (1982)	(73) Leask et al. (1981)
(10) Hammann and Ocio (1977) (4)	42) Kasten et al. (1975)	(74) Khat'sko et al. (1994)
(11) Kazei et al. (1991) (4)	43) Becher and Kalbfleisch (1973)	(75) Roser et al. (1992)
(12) Filippi et al. (1980) (4	44) Becker (1976)	(76) Murao (1988)
(13) Hammann and Manneville (1973) (4	45) Mennenga et al. (1984b)	(77) Nakajima et al. (1990)
(14) Cashion et al. (1970) (4	46) Beauvillain et al. (1977)	(78) Veenendaal et al. (1983)
(15) Cooke et al. (1971) (4	47) Als-Nielsen et al. (1975)	(79) Roser and Corruccini (1990)
(16) Hellwege and Stout (1968) (4)	48) Cooke et al. (1975)	(80) Corruccini et al. (1994)
(17) Hammann and Ocio (1980) (4)	49) Bleaney et al. (1992)	(81) Skanthakumar et al. (1990)
(18) Kappatsch et al. (1970) (5)	50) Holmes et al. (1970)	(82) Hundley et al. (1989)
(19) Cashion et al. (1968) (5	51) Brown et al. (1990)	(83) Allenspach et al. (1993)
(20) Blöte et al. (1969) (5)	52) Ellingsen et al. (1982)	(84) Wortmann and Felner (1990)
(21) Wanklyn (1973) (5	53) Skjeltorp et al. (1973)	(85) Yang et al. (1989)
(22) Abbas et al. (1974) (5-	54) Catanese et al. (1973)	(86) Clinton et al. (1991)
(23) Rossat-Mignod et al. (1972) (5	55) Fillion et al. (1980)	(87) Hodges et al. (1987)
(24) Quezel et al. (1972) (5)	56) Landau et al. (1973)	(88) Guan et al. (1993)
(25) Hulsing et al. (1978) (5	57) Skjeltorp (1977)	(89) Dunlap et al. (1987)
(26) Hulsing et al. (1983) (5	58) Wolf et al. (1961)	(90) Lynn (1992)
(27) Elmaleh et al. (1971) (5)	59) Colwell et al. (1969)	(91) Roessli et al. (1994)
(28) Metcalfe and Rosenberg (1972) (6)	60) Xu et al. (1990)	(92) Zhang et al. (1992a,b)
(29) Kockelmann et al. (1991) (6	61) Cooke et al. (1968)	(93) Rosov et al. (1993)
(30) Mensinger et al. (1993) (6	62) Hirvonen et al. (1975)	(94) MacChesney et al. (1964)
(31) Cooke et al. (1973) (6	63) Xu and Corruccini (1987)	(95) Bulman et al. (1991)
(32) Becher et al. (1973) (6	64) Bellesis et al. (1987)	

NONMETALLIC LANTHANIDE COMPOUNDS

a system formed by the lanthanide ions with a quasidoublet ground state and the nuclear spin $I = \frac{1}{2}$ (Triplett and White 1973). When neglecting the nuclear Zeeman energy, the spin Hamiltonian of this system can be written as follows

$$\mathcal{H}_{\rm S} = \sum_{i} \left(\delta_0 S_{xi} + g \mu_{\rm B} H_{0z} S_{zi} + a I_{zi} S_{zi} \right) + \frac{1}{2} \sum_{ij} K_{ij} S_{zi} S_{zj}, \tag{210}$$

where the constants g and a specify the projections of the electronic Zeeman and hyperfine interactions on the two electronic singlets. Suppose that at T = 0 the system has a ferromagnetic ground state, then the expressions for the average electron and nuclear moments within the framework of the simple mean field approximation yield the following equation for the critical temperature $T_{\rm C}$:

$$\tanh x = \left[-\frac{K_0}{2\delta_0} + x \left(\frac{a}{2\delta_0} \right)^2 \right]^{-1},$$
(211)

where

$$x = \frac{\delta_0}{2k_{\rm B}T_{\rm C}}, \qquad K_0 = \sum_j K_{ij}, \qquad K_0 < 0,$$
 (212)

and there appear two intrinsic parameters $R_e = -K_0/2\delta_0$ and $R_I = a/2\delta_0$ which determine the different regimes of magnetic ordering. If $R_I = 0$, eq. (211) has a solution only for $R_e > 1$, whereas for $R_e < 1$ no electronic ordering takes place. A finite solution always exists when $R_I \neq 0$, and for values of $R_e \ll 1$ and x > 1, the Curie temperature can be estimated from the expression

$$k_{\rm B}T_{\rm C} = \frac{\delta_0}{2} \frac{R_{\rm I}^2}{1 - R_{\rm e}}.$$
(213)

Thus, the system in question exhibits either electronic magnetism (electronic regime) or nuclear magnetism (nuclear regime) according to the ratio between the interionic coupling (exchange and dipole-dipole) and the zero field electronic level splitting. Some qualitatively similar results were obtained for more complicated systems with an excited electronic doublet and an arbitrary nuclear spin I (Andres 1973, Murao 1983). The case when R_e is only slightly less than its limiting value is often referred to as the coupled electron-nuclear regime, a small value of R_I is sufficient for k_BT_C to be close to δ_0 in order of magnitude. Examples of the nuclear regime corresponding to small values of the R_e ratio due to a large energy gap (HoVO₄, $\Delta = 21 \text{ cm}^{-1}$) or weak magnetic coupling (Cs₂NaHoCl₆, see table 5), were mentioned in sect. 3.7. The nuclear regime was also observed in HoGaG ($\delta_0 = 5.1 \text{ cm}^{-1}$) and HoAlO₃ ($\delta_0 = 5.5 \text{ cm}^{-1}$) crystals with the dominant dipole-dipole interactions. The ordering in TbGaG ($\delta_0 = 2 \text{ cm}^{-1}$), Tb₂(SO₄)₃·8H₂O ($\delta_0 = 0.61 \text{ cm}^{-1}$) and, perhaps, in

HoAlG ($\delta_0 = 3.22 \text{ cm}^{-1}$), Tb(BrO₃)₃·9H₂O ($\delta_0 = 1.04 \text{ cm}^{-1}$) corresponds to the coupled regime, but in a number of terbium compounds the energy gap δ_0 is small enough for electronic ordering to occur (see table 22 for the values of critical temperatures and references, in units of cm⁻¹ $\delta_0 = 0.66$ in TbAsO₄, 0.95 in TbVO₄, 0.92 in LiTbF₄, 0.3 in Tb(OH)₃, 0.44 in TbES, 0.35 in TbTFMS, and <1 in Tb₂O₂SO₄).

Terbium and holmium trifluorides present clear examples of different ordering regimes in singlet magnets (Holmes et al. 1970, Leask et al. 1994). There are four lanthanide ions in the orthorhombic unit cell connected in two magnetically equivalent pairs by inversion and differing only in the orientation of the local coordinate systems (see sect. 1). The low-symmetry crystal field results in the ${}^{7}F_{6}$ (Tb³⁺) and ${}^{5}I_{8}$ (Ho³⁺) ground manifolds splitting into singlet states. The spectral parameters of the Tb³⁺ and Ho³⁺ ions calculated with the crystal field parameters, obtained by Bumagina et al. (1977) in the framework of the exchange charge model, are consistent with the experimental data. It should be noted that not only the magnitude but also the correct direction of the local quantization axis of the magnetic moment can result from such calculations. The two lowest singlets form a quasidoublet with the initial splitting $\delta_0 = 0.39 \,\mathrm{cm}^{-1}$ (6.59 cm⁻¹) and the g-factor $g_{\parallel} = 17.9 \pm 0.4$ (14.92) in the TbF₃ (HoF₃) crystal (the effective spin Hamiltonian is given in eq. 123). The magnetic moment in the doublet state is in the acplane with the angle $\phi = \pm 27 \pm 2^{\circ}$ in the TbF₃ and $\pm 25 \pm 1^{\circ}$ in the HoF₃ crystals. Magnetic ordering in TbF₃ was studied with thermal (heat capacity) and magnetic (susceptibility and magnetization) measurements and using optical spectroscopy methods. This crystal was shown to be a two-sublattice canted antiferromagnet with the ferromagnetic ordering along the a-axis, and the magnetization was found to be consistent with the electronic g-factor. The constants of the dipolar fields affecting the Tb³⁺ ions are given in table 23. These lattice sums may also be used for other members of the corresponding series owing to small differences in the unit cell parameters. In the mean field approximation the singleion Hamiltonian may be written in the form

$$\mathcal{H}_{\rm S} = \delta_0 S_x + K_0 \left< S_z \right> S_z,$$

where

$$K_{0} = -(g_{\parallel}\mu_{\rm B})^{2} \left\{ \cos^{2}\phi \sum_{\lambda=1}^{4} Q_{xx}(1\lambda) + \sin 2\phi Q_{xz}(13) + \sin^{2}\phi \left[Q_{zz}(11) - Q_{zz}(12) + Q_{zz}(13) - Q_{zz}(14)\right] \right\}.$$
(214)

With the data from table 23 we obtain $K_0 = -11.1 \text{ cm}^{-1}$ and the R_e ratio is many times more than unity, thus there is electronic ordering in TbF₃. The mean field ordering temperature 4 K, due to purely dipolar interactions, almost coincides with the measured value of $T_C = 3.91$ K, but this does not indicate that the exchange interactions are negligible. The critical external magnetic field parallel to the *c*-axis induces the

Table 23 The nonzero dipolar sums $Q_{\alpha\beta}(\lambda\lambda')$ in units of $4\pi/3v^a$ in the DyVO₄ (a), LiTbF₄ (b) and TbF₃ (c) crystals ($x \parallel a$, $y \parallel b, z \parallel c$)

α,β	a/b/c	$\lambda, \lambda' = 1, 1$		$\lambda, \lambda' = 1, 2$		$\lambda, \lambda' = 1, 3$		$\lambda, \lambda' = 1, 4$	
		$r_{\lambda} - r_{\lambda'}$	$Q_{lphaeta}(\lambda\lambda')$	$r_{\lambda} - r_{\lambda'}$	$Q_{\alpha\beta}(\lambda\lambda')$	$r_{\lambda}-r_{\lambda'}$	$Q_{lphaeta}(\lambda\lambda')$	$r_{\lambda}-r_{\lambda'}$	$Q_{lphaeta}(\lambda\lambda')$
<i>x</i> , <i>x</i>	a	0, 0, 0	0.8066	0.5, 0.5, 0.5	1.1574	0, 0.5, 0.25	-1.7605	0.5, 0, 0.75	4.6134
	b	0,0,0	2.2627	0.5, 0.5, 0.5	0.0985	0, 0.5, 0.25	-0.9885	0.5, 0, 0.75	1.8232
	с	0,0,0	0.2817	0.5, 0, 0.5-2z	4.2092	2x, 0.5, -2z	0.2664	0.5–2 <i>x</i> , 0.5, 0.5	0.0625
уу	а	0,0,0	0.8066	0.5, 0.5, 0.5	1.1574	0, 0.5, 0.25	4.6134	0.5, 0, 0.75	-1.7605
	b	0, 0, 0	2.2627	0.5, 0.5, 0.5	0.0985	0, 0.5, 0.25	1.8232	0.5, 0, 0.75	-0.9885
	с	0, 0, 0	0.0250	0.5, 0, 0.5-2z	-1.9124	2x, 0.5, -2z	3.0101	0.5-2x, 0.5, 0.5	2.5237
<i>z</i> , <i>z</i>	a	0, 0, 0	1.3868	0.5, 0.5, 0.5	0.6852	0, 0.5, 0.25	0.1471	0.5, 0, 0.75	0.1471
	b	0, 0, 0	-1.5254	0.5, 0.5, 0.5	2.8030	0, 0.5, 0.25	2.1653	0.5, 0, 0.75	2.1653
	с	0, 0, 0	2.6933	0.5, 0, 0.5-2z	0.7032	2x, 0.5, -2z	-0.2765	0.5-2x, 0.5, 0.5	0.4138

^a $v=a^2c$ for tetragonal lattices; the single independent nondiagonal element in the TbF₃ lattice $Q_x(13) = -0.1072 (4\pi/3v), v=abc$; the lattice constants are given in sect. 1.

metamagnetic transition at T=0 with the spin-flip in the $\lambda=2$ and 4 sublattices. When taking into account again only dipolar interactions, this field equals

$$H_{0m} = \frac{g_{\parallel} \mu_{\rm B}}{2\sin\phi} \left\{ \cos^2\phi \left[Q_{xx}(12) + Q_{xx}(14) \right] - \sin^2\phi \left[Q_{zz}(12) + Q_{zz}(14) \right] \right\},\tag{215}$$

and estimation of eq. (215) gives a value of 14 kOe close to the measured value of 13.1 ± 0.5 kOe at 1.1 K. This confirms the electronic regime of the magnetic ordering.

With the HoF₃ parameters we obtain $K_0 = -9.85 \text{ cm}^{-1}$ from eq. (214) and the ratio $R_e = 0.74$ is below the threshold value for inducing the ordering of the electronic system. Thus the magnetic ordering in the HoF₃ crystal, studied by means of neutron diffraction and inelastic neutron scattering by Brown et al. (1990) and Leask et al. (1994) at temperatures below and above $T_C = 0.53$ K, is of a coupled electron-nuclear type. The spin configuration of HoF₃ in the ordered phase is the same as in the TbF₃ crystal, with the holmium magnetic moments of $5.7\mu_B$ at 70 mK. The magnetic moment involves the enhanced nuclear and the electronic Van Vleck contribution (see eq. 127) $M = 4.1\mu_B$. The latter was derived from magnetic susceptibility measurements by Bleaney et al. (1988c). The difference in the nature of magnetic ordering in TbF₃ and HoF₃ is manifested in the temperature dependences of the dc susceptibility at $T < T_C$. Due to the dominating dipolar interactions in TbF₃ $\chi_{aa} = 1/D = \text{const.}$, and in HoF₃ χ_{aa} has a maximum at T_C similar to that observed in antiferromagnets.

The hexagonal lattices which are isostructural with lanthanide hydroxides, trichlorides, tribromides, ethylsulfates and trifluoromethane sulfonates, contain two magnetically equivalent lanthanide ions per unit cell. The structure is such that the nearest and nextnearest neighbours are significantly closer than other neighbours and the most effective dipole-dipole interaction connects the nearest neighbours in chains along the crystal symmetry axis. Many of the magnetic properties are strikingly different for the same type of lanthanide ion with different ligands. This is caused mainly by the difference in lattice constants which shifts the dominant magnetic interactions from those almost purely dipolar for ethylsulfates and trifluoromethane sulfonates, to the predominantly nondipolar for hydroxides which are most concentrated. The light lanthanide hydroxides contain antiferromagnetic chains with weak interchain coupling. A short-range order effect on the susceptibility of the Nd(OH)₃ was observed by Ellingsen et al. (1982) at temperatures slightly above the transition point. Dipolar interaction dominates in the case of heavy lanthanides with large magnetic moments, and $Tb(OH)_3$ (see table 11), $Ho(OH)_3$ $(g_{\parallel} = 15.5)$ and Dy(OH)₃ $(g_{\parallel} = 19)$ are 3D-Ising ferromagnets. In the trichlorides with lattice parameters somewhat larger than those of hydroxides there is a strong competition between dipolar and nondipolar interactions. In particular the antiferromagnetic ordering in NdCl₃ is dominated by the nondipolar XY coupling (see table 11). As a result of the cancellation between the magnetic dipolar and exchange interactions for the first and second neighbours the dipolar interactions between more distant neighbours may be of importance.

The transition temperatures obtained with the mean field approximation are always overestimated. The deviations from the experimental data are especially remarkable for systems with prevailing dipolar interactions when there are no fitting parameters in the theory. For example, in TbES a simple molecular field theory gives $T_{\rm C}({\rm MFA}) = 0.649 \,{\rm K}$ and only a small change in $T_{\rm C}$ results with the hyperfine interaction, $T_{\rm C}$ (MFA HF) = 0.651 K. Attempting to take into consideration the peculiarities of the ethylsulfate lattice structure Hirvonen et al. (1975) dealt with two- and threeparticle cluster approximations (separating the nearest neighbours along the chains) and obtained the values $T_{\rm C}$ (MFA CL) = 0.53 K and 0.40 K, respectively, which are still far from the measured Curie temperature of 0.24 K. In DyES $T_{\rm C}({\rm MFA}) = 0.259$ K, $T_{\rm C}$ (MFA CL) = 0.172 K; by using the exact theoretical results for the one-dimensional Ising system with the nearest-neighbour interactions only Cooke et al. (1968) found $T_{\rm C} = 0.154 \, {\rm K}$ for the system of dipolar coupled Ising chains, which is much closer to the experimental Curie temperature of 0.118 K (Frowein and Kotzler 1976). The mechanism of unexpected uniaxial antiferromagnetic ordering in HoES ($g_{\parallel} = 15.4$), observed by Xu and Corruccini (1987), who had assumed it to be due to the strong hyperfine interaction, is not clear. It should be noted that even in the absence of lattice anisotropy in the cubic $Cs_2NaR(NO_2)_6$, $Cs_2NaDyCl_6$, and $Cs_2NaErCl_6$ crystals with primary dipolar interactions, the mean-field critical temperatures exceed those observed by Roser and Corruccini (1990) and Roser et al. (1992) roughly twice and even more (the observed ordering temperatures for compounds with different lanthanide ions scale approximately as the square of the effective magnetic moment, as would be expected for dipolar interactions). Gehring et al. (1976a) analyzed the magnetic properties of the two singlet $TbVO_4$ and TbAsO₄ magnets using the transverse Ising model with the experimentally determined parameters of exchange and dipolar interactions, solved in a random phase approximation. They obtained a remarkably better agreement between the calculated and measured temperatures of the antiferromagnetic ordering than in the molecular field theory. The correct estimations of the Curie temperatures in dipolar magnets were obtained only in the Monte-Carlo simulations by Favorskii (1985) for DyES, Jensen and Kjaer (1989) and Xu et al. (1992) for LiHoF₄.

The lanthanide *bromates* have a pseudohexagonal structure differing from that of the ethylsulfates in two possible orientations of the $(BrO_3)^-$ anions in the high-temperature phase. Ferromagnetic ordering was observed for the same lanthanide ions as in ethylsulfates, but in spite of the similarity of trigonal $[R(H_2O)]_9^{3+}$ cells, the Dy³⁺ ions have different ground states with $g_{\parallel} = 10.8$, $g_{\perp} = 0$ in the DyES, and $g_{\parallel} = 7.2$, $g_{\perp} = 11.0$ in the bromate. The Curie temperature $T_C = 0.14$ K due solely to dipolar interactions calculated by Simizu et al. (1986) for the dysprosium bromate is close to the observed value.

The hexagonal lanthanide oxysulfides R_2O_2S and oxyselenides R_2O_2Se order antiferromagnetically due to strong exchange interactions between the nearest neighbours ($V_S \approx 43 \text{ Å}^3$). The complicated magnetic structures, differing in propagation vectors and orientations of the magnetic moments, were described by Ballestracci et al. (1968), Rossat-Mignod et al. (1972), and Abbas et al. (1974, 1977).

Magnetic properties of the lanthanide *oxysulfates* $R_2O_2SO_4$ were thoroughly studied by Hulsing et al. (1978, 1980, 1983), Hulsing and Kasten (1979), and Kahle and Kasten (1983). These compounds exhibit interesting low temperature properties due to the unique orthorhombic crystal structure with lanthanide–oxygen double layers perpendicular to the crystallographic *c*-direction. Strong antiferromagnetic exchange interactions connect closely packed lanthanide ions belonging to the same layer, and the two-dimensional ordering determines the peculiarities of the specific heat, the magnetic susceptibility and the Zeeman effect in the optical absorption spectra. With the exception of $Gd_2O_2SO_4$, all substances exhibit planar Ising antiferromagnetic behaviour with the directions of the magnetic moments fixed along their easy axis (see table 11).

We cannot consider here in detail the problem of metamagnetic transitions (for a review see Stryjewski and Giordano 1977). However, it should be noted that the existence of intermediate phases, with the magnetization successively increasing in several steps, is a common feature of systems with strong dipolar interactions (Kasten and Kahle 1986). The RO_2SO_4 compounds may serve as examples. In external magnetic fields the $Ho_2O_2SO_4$ canted antiferromagnet and the $Dy_2O_2SO_4$ collinear antiferromagnet undergo two successive metamagnetic transitions to the paramagnetic saturated configuration via an intermediate ferrimagnetic state with a tripled magnetic unit cell and a magnetization of one-third of the saturation magnetization.

The coordination polyhedron of each lanthanide ion in the tetragonal $R_2Ge_2O_7$ pyrogermanates is a distorted pentagonal bipyramid with a D_{5h} symmetry and the symmetry axis nearly parallel to the tetragonal *c*-axis. Due to this unique point symmetry the magnetic properties of pyrogermanates are expected to be of interest.

In the lanthanide RAIO₃ *aluminates* and RCoO₃ *orthocobaltites* (where Co^{3+} is diamagnetic) with a deformed perovskite structure there is a strong competition between the antiferromagnetic exchange and dipolar interactions due to the close packing of the

magnetic R ions ($V_s \approx 52-60 \text{ Å}^3$). There are four molecules per unit cell and a variety of antiferromagnetic structures occur in compounds with different lanthanide ions.

The lanthanide orthovanadates, orthophosphates and arsenates with the zircon structure are of interest on account of the variety of crystallographic transformations and magnetic arrangements they display at low temperatures. The dipolar and exchange interactions between the nearest neighbours in RMO₄ (M=V, P, As) crystals are comparable in magnitude. The observed magnetic structures can be described by considering four Bravais sublattices with the magnetic moments μ_{λ} ($\lambda = 1, 2, 3, 4$). In the high-temperature tetragonal phase with the (100), (010), (001) vectors of translations, the corresponding basis vectors are equal to $r_1 = (000)$, $r_2 = (\frac{1}{2} \frac{1}{2})$, $r_3 = (0 \frac{1}{2} \frac{1}{4})$, $r_4 = (\frac{1}{2} 0 \frac{3}{4})$. For the GdAsO₄, GdVO₄, YbVO₄ ($g_{\parallel} = 6.5, g_{\perp} = 0.85$, Radhakrishna et al. 1981), DyPO₄, HoPO₄, HoAsO₄, TbPO₄ (in the range of temperatures $T_N = 2.28 \text{ K} > T > T_D = 2.13 \text{ K}$, Mensinger et al. 1993) compounds $\mu_1 = \mu_2 = -\mu_3 = -\mu_4$ (two-sublattice Heisenberg and Ising antiferromagnets) with μ_{λ} parallel to the *c*-axis. In the gadolinium compounds the exchange interactions are dominant, the dipolar field

$$H_{\rm dz} = \sum_{\lambda'} Q_{zz}(\lambda, \lambda') \, \mu_{\lambda' z},$$

estimated with the data from table 23 for GdVO₄ does not exceed 15% of the exchange field. The TbAsO₄ and TbVO₄ crystals are the two-sublattice Ising antiferromagnets belonging to the magnetic symmetry Fdd'd' (Gehring et al. 1976a) with the same relations between the μ_{λ} magnetic moments as above but perpendicular to the *c*-axis (see table 11), and the directions of the magnetization are determined by spontaneous strains in the structural domains. The four-sublattice DyVO₄ and DyAsO₄ antiferromagnets (the magnetic group is P₁nm*a*) have a layered magnetic structure: $\mu_1 = -\mu_2 = \pm \mu_3 = \mp \mu_4$ with the upper or lower signs when μ_{λ} is parallel to the [010] or [100] direction, respectively (in this case the dipole field H_{dy} (or H_{dx}) reaches its maximum, see table 23). No indication of a canted magnetic structure in DyAsO₄ as suggested by neutron diffraction (Will et al. 1971) was observed by Kasten (1980). The TbPO₄ crystal at temperatures lower than the crystallographic phase transition point of 2.13 K becomes a canted antiferromagnet with the magnetic moments tilted off the *c*-axis, which implies monoclinic symmetry (Muller et al. 1993).

The lithium lanthanide double fluorides represent the most exhaustively studied set of compounds which contains the LiHoF₄, LiTbF₄ Ising ferromagnets and the LiErF₄, LiDyF₄ ($g_{\parallel} = 1.1, g_{\perp} = 9.2$) antiferromagnets with the dominant dipolar interactions (see table 11). Similar to crystals with the zircon structure described above, the magnetic structures of the tetragonal double fluorides are formed by four Bravais sublattices with the same basis vectors \mathbf{r}_{λ} ($\lambda = 1, ..., 4$) but, as may be seen in table 23, the dipolar fields in these lattices are quite different. The ion magnetic moments $\boldsymbol{\mu}_{\lambda}$ in the LiHoF₄ and LiTbF₄ crystals are all parallel to the *c*-axis. The contribution, due to the dipolar interactions, to the molecular field constant in the ferromagnetic domains with the zero demagnetizing field, is obtained from the data given in table 23: $\Lambda_{dzz} + 4\pi/3 = 5.85$. The constants of the exchange fields, defined in eq. (199), have the opposite sign and do not exceed two by the modulus (Cooke et al. 1975, Holmes et al. 1975, Beauvillain et al. 1980b), the corresponding pair exchange integrals $A_{zz}(i, j)$ are in the range from 2,5 to 4 (10^{-3} cm⁻¹). The ground-state spin arrays in LiErF₄ and LiDyF₄ are also determined by the prevailing dipolar interactions; a layered antiferromagnetic ordering in the basis lattice plane along the crystallographic axes a or a' is consistent with the minimum of the dipolar energy, and similar to the spin configuration in the DyVO₄ crystal, the magnetic moments of the sublattices satisfy the equalities: $\mu_1 = -\mu_2 = \pm \mu_3 = \mp \mu_4$ with the upper or lower signs when μ_{λ} are parallel to the [010] or [100] direction, respectively (Misra and Felsteiner 1977, Mennenga et al. 1984a). The mean field Néel temperatures, corresponding to the purely dipolar internal field $H_{d1} = 20.9 \,\mu_1/a^2c$ (see table 23), are more than twice the measured ones. There should be a considerable exchange interaction between the lanthanide ions, but the existing estimates are to be further elaborated.

The DyOCl and TbOCl *oxychlorides* belonging to the tetragonal structure type PbFCl (n=2, and for each lanthanide ion there are four magnetic neighbours at 3.55 Å and four neighbours at 3.92 Å) have relatively high Néel temperatures due to the strong exchange and dipolar interactions at short distances between the nearest neighbours and the big magnetic moments $10.5\mu_{\rm B}$ and $9.84\mu_{\rm B}$ of Dy³⁺ ($\mu \perp c$) and Tb³⁺ ($\mu \parallel c$) ions, respectively. The magnetic cell is twice the chemical cell in DyOCl, and the precise magnetic superstructure of TbOCl is unknown (Elmaleh et al. 1971).

Syntheses of the high- T_c superconductors involve rare-earth oxides in the initial stage, and minute amounts of these materials may remain in the final products. Heavy lanthanide R₂O₃ sesquioxides crystallize in the cubic C-modification. Due to a large number of nonequivalent magnetic ions (eight with the C₂ point symmetry and 24 with C_{3i} symmetry) in the unit cell and in spite of the small interionic distances between the nearest neighbours ($V_S \approx 40 \text{ Å}^3$), the transition temperatures are not high. On the grounds of the heat capacity and susceptibility measurements of the Er₂O₃ samples, Tang et al. (1992) suggested that the antiferromagnetic ordering at 3.3 K occurred only among the Er ions in the trigonal crystal field (the magnetic-entropy change was found to be 0.75 R ln 2).

The specific magnetic properties of the *copper oxides* RBa₂Cu₃O_{7- δ} (R=lanthanide ion), in which the magnetic ordering may coexist with the superconductivity at characteristic temperatures, are conditioned by their layered structure. The tetragonal ($\delta \approx 1$, $a \approx 3.86$ Å), or nearly tetragonal ($\delta \approx 0$, $b-a \approx 0.06$ Å) chemical unit cell contains only one lanthanide ion, and the separation of the neighbouring R-ions along the *c*-axis is approximately three times that along the *a*,*b* axes. There are three copper-oxygen layers which are stacked along the *c*-axis. Two of these layers have oxygen ions between the Cu ions in both the *a* and *b* crystallographic directions (the CuO₂ layers), the third layer has oxygen ions along only one axis. This is the so-called "chain" layer, and the oxygen concentration can be readily varied in this layer from full occupancy ($\delta = 0$) to full depletion ($\delta = 1$). With the notable exception of the Pr compounds, the antiferromagnetic ordering in the lanthanide sublattice takes place at temperatures lower than 2.5 K and in the tetragonal phase it coexists with the antiferromagnetic ordering in the Cu sublattice. A number of recent measurements of the specific heat, magnetization, and magnetic structures, have demonstrated that there is a significant exchange coupling in the *ab*-planes along with the dipole-dipole interactions.

These experiments stimulated investigations of the effects due to the dipolar interactions in the two-dimensional systems. In particular, MacIsaac et al. (1992) have shown, by means of the Monte-Carlo simulations, that the Nd and Dy compounds may be considered as belonging to the universality class of the two-dimensional Ising antiferromagnets with short-range coupling even when taking into account the long-range dipolar interactions. It should be mentioned that Corruccini and White (1993) did not find any long-range order for the dipolar square lattice in the spin-wave approximation. The necessity of including exchange interactions into the consideration of the magnetic ordering in the R123-compounds was emphasized by Anders and Volotskii (1992) on the grounds of the results of magnetic structure calculations according to the Luttinger-Tisza method. The estimations of the exchange constants for the intraplanar coupling between the nearest neighbours $[J_{\parallel} = 1.1 \text{ K} (\text{DyBa}_2\text{Cu}_3\text{O}_7, g_{\parallel} = 14.5), 2.0 \text{ K} (\text{DyBa}_2\text{Cu}_4\text{O}_8, g_{\parallel} = 11.8),$ 3.6 K (NdBa₂Cu₃O₇, $g_{\parallel} = 2.28$)], obtained from the comparison of the calculated and measured Néel temperatures, are not in contradiction with similar data for other crystals (see table 11). The two-dimensional (2D) character of the magnetic ordering is the most pronounced in the bilayered Dy₂Ba₄Cu₇O₁₅ compound (Zhang et al. 1992a,b) and in the $DyBa_2Cu_4O_8$ oxide where the neighbouring *ab*-layers are shifted along the *b*-axis by half of a lattice constant and the interplanar coupling is essentially diminished. Twodimensional correlations of the magnetization fluctuations appear to be present in the neutron scattering at $T > T_N$.

The propagation vectors of different spin configurations in the orthorhombic R-Ba-Cu-O oxides are (a) $\left[\frac{1}{2} 0 \frac{1}{2}\right]$ for R=Er, (b) $\left[\frac{1}{2} \frac{1}{2} \frac{1}{2}\right]$ for R=Gd, Nd, Dy, (c) $\left[\frac{1}{2} \frac{1}{2} 0\right]$, and (d) $\left[\frac{1}{2} 0 0\right]$ (see fig. 23). The magnetic moments of Pr, Gd, Nd and Dy are perpendicular to the *ab*-plane and those of Er are parallel to the *b*-axis. The magnitudes of the moments and their directions are in agreement with the results of the crystal



Fig. 23. Magnetic structures in the RBa₂Cu₃O_{7- δ} crystals. The propagation vectors equal (a) $(\frac{1}{2}0\frac{1}{2})$; (b) $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$; (c) $(\frac{1}{2}\frac{1}{2}0)$; (d) $(\frac{1}{2}00)$.

field calculations, thus the low Néel temperature in the HoBa₂Cu₃O₇ oxide is due to the singlet ground state (with the crystal field parameters of Furrer et al. (1988) the initial splitting of the non-Kramers quasidoublet equals ~4 cm⁻¹ and $g_b = 12.4$). The low-temperature magnetic structures and the character of the critical behaviour correlate with the oxygen concentration. An essential rounding of the magnetic transition, and drastic effects on the magnetic correlations, controlled by the density of charge carriers in the superconducting CuO₂ planes, were observed in the change from the orthorhombic (superconducting) to tetragonal (insulating) lattice structure (Allenspach et al. 1993, Clinton et al. 1993), indicating that the exchange interactions are strongly influenced by the "chain" layer oxygen. More recently Clinton et al. (1995) have found the diminishing longe-range magnetic ordering in the de-oxygenated $ErBa_2Cu_3O_{7-\delta}$ compounds with the Néel temperatures from 0.62 K (δ =0), through 0.48 K (δ =0.4), to less than 0.06 K ($\delta = 1$). Some magnetic structures exhibit evolution with varying oxygen deficiency, from (b) to (c) for Gd and from (a) to (d) for Er compounds. Structures of the (b) and (c) type may coexist in the Dy compounds, and (a)- and (d)type structures may coexist in the Er compounds (De'Bell and Whitehead 1991, Clinton et al. 1991).

For completeness we include the data on the compounds with Pr^{4+} and Tb^{4+} ions listed in table 22. The origin of the enhanced exchange in these systems and also in $PrBa_2Cu_3O_x$ is unclear as yet.

Lanthanide compounds are adequate model systems for proving the theories of critical phenomena in crystals exhibiting phase transitions. Modern theories are based on the renormalization group (RG) approach. For each universality class of critical behaviour there is an upper spatial marginal dimensionality d^* when the RG-equations can be solved exactly. If the system dimensionality d is less than d^* the non-classical power-law dependences occur near the critical point $T_{\rm C}$. In magnetic materials with short-range exchange interactions $d^*=4$, and the magnetization $m=M/M_{\rm S}$, the susceptibility $\chi^{(T)}$ (in units of $\chi_0 = M_{\rm S}/H_{\rm S}$) and the specific heat $C_{\rm H}$ (in units of $V_{\rm m}M_{\rm S}H_{\rm S}/T_{\rm C}=R$, where $V_{\rm m}$ is the molar volume, $M_{\rm S}=N_{\rm A}g\mu_{\rm B}S/V_{\rm m}$ is the magnetization maximum value and $H_{\rm S}=k_{\rm B}T_{\rm C}/g\mu_{\rm B}S$) as functions of the reduced temperature $t=(T-T_{\rm C})/T_{\rm C}$ and magnetic field $h=H_0/H_{\rm S}$ can be written as follows

$$m(-t) = \widetilde{B}(-t)^{\beta}, \quad t < 0, \quad h = 0,$$
 (216)

$$m(h) = \widetilde{D} \left| h^{1/\delta} \right|, \qquad t = 0, \tag{217}$$

$$\chi(t) = \widetilde{\Gamma} t^{-\gamma} \qquad t > 0, \qquad h \to 0, \tag{218}$$

$$C_{\rm H} = \widetilde{A}t^{-\alpha}, \qquad t > 0, \qquad h = 0. \tag{219}$$

The critical exponents α , β , γ , δ , are expressed in the perturbation expansion in terms of the parameter $\varepsilon = d^* - d$, and the expansion coefficients depend upon an order parameter dimensionality. In the diluted systems $d^* = 6$, in tricritical points and in three-dimensional dipolar-coupled Ising ferromagnets $d^* = 3$. Among lanthanide compounds uniaxial and

isotropic ferro- and antiferromagnets with order parameters of different dimensionality may be observed.

There exist also systems with multicritical points in their phase diagrams and with complex crossover behaviour from one set of critical exponents to another when the range of reduced temperature is large enough. Examples of mixed and diluted systems will be considered in the last section of this review. Here we discuss only some results of the precise experiments demonstrating the unique features of the phase transitions in dipolar uniaxial ferromagnets.

Magnetic dipole-dipole interactions occur in all real magnetic materials, but in the lanthanide compounds, as can be seen in table 11, their role is vital since the gain in energy due to the spontaneous symmetry breaking $(k_{\rm B}T_{\rm C})$ equals the dipolar energy within an order of magnitude. The dipolar interaction exerts a most profound effect on the critical behaviour of the Ising ferromagnet. In this case the spatial dispersion of the order parameter susceptibility at long wavelengths is described by the equation (Griffin and Litster 1979)

$$\chi(t, \boldsymbol{q}) = \chi(t, 0) \left[1 + \xi^2 (q^2 - bq_z^2) + g^2 \xi^4 \left(\frac{q_z^2}{\xi^2 q^2} \right) \right],$$
(220)

where $\xi \sim |t|^{-1/2}$ is the correlation length, g and b are functions of the dipolar and the short-range couplings. The mean-field approximation is invalid when the order parameter $m \sim |t|^{1/2}$ becomes comparable to the root-mean squared fluctuations

$$\left<\Delta m^2\right>^{1/2} \sim \frac{k_{\rm B}T_{\rm C}\chi(t,0)}{V_{\rm C}}$$

(the Ginzburg criterion). The correlation volume $V_{\rm C}$ in accordance with eq. (218) grows as ξ^2 along the z axis (the effective longitudinal correlation length ξ_{\parallel} equals $g\xi^2$) and as ξ in other directions, $\chi(t,0) \sim |t|^{-1}$ and we obtain

$$\frac{\left\langle \Delta m^2 \right\rangle}{m^2} \sim \left| t \right|^{(d-3)/2},$$

where the marginal dimensionality $d^*=3$ separates mean-field and nonclassical critical behaviour. At the marginal dimensionality, Larkin and Khmel'nitskii (1969) predicted a logarithmic correction term to the Landau-like behaviour due to highly anisotropic fluctuations in the three-dimensional dipolar Ising model. In this case the singular parts of the spontaneous magnetization, the critical isotherm, the low-field magnetic susceptibility and the specific heat are given by the following expressions

$$m(-t) = B(-t)^{1/2} \left| \ln(-t) \right|^{1/3}, \qquad t < 0, \quad h = 0,$$
(221)

$$m(h) = D |h|^{1/3} |\ln h||^{1/3}, \qquad t = 0,$$
(222)
$$\chi(t) = \Gamma t^{-1} \left| \ln t \right|^{1/3}, \qquad t > 0, \quad h \to 0,$$
(223)

$$\chi(t) = \Gamma'(-t)^{-1} \left| \ln (-t) \right|^{1/3}, \qquad t < 0, \quad h \to 0,$$
(224)

$$C_{\rm H} = A \left| \ln t \right|^{1/3}, \qquad t > 0, \quad h = 0,$$
 (225)

$$C_{\rm H} = A' \left| \ln \left(-t \right) \right|^{1/3}, \quad t < 0, \quad h = 0.$$
 (226)

According to RG-calculations performed by Aharony and Halperin (1975), Brezin (1975), and Aharony and Hohenberg (1976), eqs. (221)–(226) are to be supplemented with the universal ratios among the critical amplitudes

$$\frac{A}{A'} = \frac{1}{4}, \qquad \frac{\Gamma}{\Gamma'} = 2, \quad R_x = \frac{\Gamma B^2}{D^3} = \frac{3}{2}, \quad R_c = \frac{A\Gamma}{B^2} = \frac{1}{6}$$

and also with the asymptotic relation between these amplitudes and that of the correlation length

$$g\xi^4 t^2 C_{\rm H} = \frac{3k}{32\pi} \left| \ln|t| \right|. \tag{227}$$

In many high-precision experiments with the lanthanide crystals, where the magnetic ordering is unambiguously determined by the dipole-dipole interactions, it has been shown that the critical exponents are really very close to their classical values. Beauvillain et al. (1975) have found the susceptibility exponent $\gamma = 1.01$ in an ErCl₃·6H₂O crystal with the exchange energy not exceeding 20% of the dipolar energy ($g_z = 13.6, g_{\perp} < 1$), some other examples are presented in table 24. For dipolar Ising ferromagnets DyES, LiHoF₄, canted ferromagnet TbF₃ and Ising ferromagnet LiTbF₄ with the initial ground state splitting $\delta_0 \approx 0.5 k_B T_C$, the logarithmically modified power laws (221)-(226) give a better description of the experimental data than the simple power laws (216)-(219) over a wide range of reduced temperature $(10^{-4}-10^{-3} < t < 10^{-2}-10^{-1})$. The first clear experimental verification of the RG-theory was obtained when examining the predicted amplitude relations. Ahlers et al. (1975) measured the logarithmic corrections to the Landau specific heat for LiTbF₄ and the corresponding amplitude ratio was found to be $A/A' = 0.244 \pm 0.009$, in excellent agreement with the predicted value. Als-Nielsen (1976) found that the amplitude ratio of the susceptibility above and below $T_{\rm C}$ had the meanfield value of two and confirmed the relation (227) with the neutron scattering data. Some examples of the experimental verification of the R_x ratio are presented in table 24. Beauvillain et al. (1980a) obtained the value of $(7.8\pm0.75)^{-1}$ for the R_c ratio. Note that the dipolar critical behaviour occurs only at sufficiently small reduced temperatures. Frowein et al. (1982) measured the effective critical exponent

$$\gamma_{\rm eff} = \frac{\mathrm{d}\ln\chi^{-1}(t)}{\mathrm{d}\ln t}$$

of the zero-field susceptibility for the LiTbF₄ and DyES crystals in a broad range of reduced temperatures, $10^{-3} \le t \le 40$, and observed a crossover from $\gamma_{\text{eff}} \approx 1.05$ to the

NONMETALLIC LANTHANIDE COMPOUNDS

	LiHoF ₄ ^a	DyES ^b	LiTbF ₄ °	TbF ₃ ^d
<i>T</i> _C (K)	1.5256-1.538	0.1182	2.8707-2.891	3.967
81	13.95	10.8	17.8	15.7
$M_{\rm s}({\rm G})$	900	85	1130	1470
$H_{\rm S}({\rm Oe})$	3260	325	4810	7520
χ ₀	0.2761	0.2615	0.2347	0.1956
В	1.516	0.89	1.77-1.65	1.56
\widetilde{B}		0.96	1.71	1.60
β	0.355	0.42	0.385	0.39
Г	1.00	2.5	0.91	1.171
$\widetilde{\Gamma}$	1.32	2.9	1.25	1.636
γ	1.05	1.07	1.065	1.04
D	1.141	1.09	1.23	1.27
\widetilde{D}		3.20		1.73
δ		2.8		3.5
R _x	1.546	1.529	1.5	1.400

 Table 24

 Critical exponents and critical amplitudes for Ising dipolar ferromagnets

^a Beauvillain et al. (1978a,b), Griffin et al. (1980).

^b Frowein and Kotzler (1976), Kotzler (1980).

^c Ahlers et al. (1975), Frowein et al. (1979), Griffin and Litster (1979), Beauvillain et al. (1980a).

^d Brinkmann et al. (1978).

mean-field value 1 through a maximum at $t \approx 1$. Such a behaviour of the critical exponents of the uniaxial dipolar ferromagnets is in agreement with the RG-calculations performed by Frey and Schwabl (1990).

4.3. Electric field effects

If the point symmetry group of the lanthanide ion does not possess an inversion, the magnetization linear in an external electric field may be observed, and the dielectric susceptibility of the sample may be also radically affected by an external or internal magnetic field. Electric field effects on the EPR spectra of the lanthanide ions in insulators are well known (see, for example, Sakharov 1979, 1980), and here we shall consider only the alteration of the dielectric properties of the crystal due to the ordering in the lanthanide subsystem. Dielectric measurements are often used to plot the phase boundaries of the lanthanide magnets in the magnetic field. The energy of the lanthanide ion in the quasistatic electric field is presented in eq. (9). The effective even dipole moment of the ion can be written as follows

$$D_{\alpha} = D_{\alpha}^{(d)} + D_{\alpha}^{(e)} + D_{\alpha}^{(i)} = \sum_{p,q} b_{p,\alpha}^{q} O_{p}^{q},$$
(228)

where p=2, 4, 6. It operates within the space of the 4f-shell wave functions and consists of the three terms corresponding to the direct interaction with the local electric field $(D^{(d)})$, with point electric dipoles of the polarized lattice ions $(D^{(e)})$ and with the ion displacements $(D^{(i)})$. The explicit form of the proper dipole moment $D^{(d)}$ is obtained by means of perturbation theory in the second order in the sum of the ion energy in the odd crystal field, mixing the states of the opposite parity, and the ion dipole moment $D = -e \sum r$. It should be noted that the high-frequency dipole moment $D^{(d)} + D^{(e)}$ determines the intensities of the radiative electric dipole transitions between the 4f-states. In crystals with an inversion point, the ionic contribution $D^{(i)}$ due to the lattice deformation in the electric field is given by the second term in eq. (19) where we are to insert the sublattice displacements

$$w_{\alpha}(\lambda) = \frac{e}{v} \sum_{\lambda'} a_{\alpha\beta}^{-1}(\lambda, \lambda') q(\lambda') E_{0\beta}, \qquad (229)$$

obtained from eq. (27). In this case the matrix $a_{\alpha\beta}(\lambda,\lambda')$ corresponds to the dynamical matrix of the lattice that determines the frequencies of the odd vibrations with the zero wave vector. Renormalization of the parameters of the effective dipole moment due to the phonon exchange between the lanthanide ions, may be carried out similarly to the renormalization of the electron-deformation interaction considered in sect. 2.5.

As an example of the interpretation of experimental data we shall discuss the dielectric susceptibility of the Ising ferromagnet LiHoF₄ in the critical region. The z- and x-, y-components of the electric field transform according to $A_u(\Gamma_2)$ and $E_u(\Gamma_{34})$ irreducible representations of the double fluoride factor group C_{4h}, respectively (the compatible irreducible representations of the point group S₄ of the lanthanide ions are shown in brackets). Projecting the operator (9) onto the ground Γ_{34} doublet with the wave functions $|\Gamma_3\rangle$, $|\Gamma_4\rangle$ of the Ho³⁺ ion, we obtain the effective spin-Hamiltonian in the following form

$$\mathcal{H}_{\rm S} = g_{\parallel} \mu_{\rm B} H_z S_z + A I_z S_z + \gamma E_z S_x, \tag{230}$$

where the magnetic and electric interactions are represented by the orthogonal pseudospin operators,

$$\gamma = 2 \left| \left< \Gamma_3 \right| - \sum_{p,q} b_{p,z}^q O_p^q \left| \Gamma_4 \right> \right|,$$

and A = 0.445 K (Magarino et al. 1980) is the constant of the hyperfine interaction, nuclear spin $I = \frac{7}{2}$. In the mean field approximation, and with the zero external magnetic field, the single ion dielectric susceptibility is found directly from the partition function; it is

$$\chi_{\rm E} = \frac{\gamma^2}{2} \sum_{m=1/2}^{7/2} \frac{1}{W_m} \sinh \frac{W_m}{2k_{\rm B}T} \left(\sum_{m=1/2}^{7/2} \cosh \frac{W_m}{2k_{\rm B}T} \right)^{-1}, \tag{231}$$

where $W_m = 4k_BT_C \langle S_z \rangle + mA$. Above T_C eq. (231) reduces to the usual Curie law, at low temperatures χ_E reduces because of the change in the populations of the hyperfine



Fig. 24. Temperature dependence of the dielectric susceptibility in LiHoF_4 . The circles are experimental data, the full and dashed curves represent the theoretical results (Page et al. 1984a).

sublevels. The parameters of the electric dipole moment have been calculated by Malkin (1987) with the exchange charge model:

 $b_{2,z}^2 = -0.887, \qquad b_{2,z}^{-2} = 0.343, \\ b_{4,z}^2 = 0.718, \qquad b_{4,z}^{-2} = -2.437, \\ b_{6,z}^2 = -0.097, \qquad b_{6,z}^{-2} = 0.105, \\ b_{6,z}^6 = 0.494, \qquad b_{6,z}^{-6} = -0.007, \end{cases}$

in units of 10^{-30} C m, and the main contributions are from the lattice deformation, the electronic terms being by an order of magnitude smaller. For two Ho ions in the unit cell, the dipole moments have different signs. With the parameters $b_{p,z}^q$ presented above we obtained $\gamma = 0.61 \ 10^{-31}$ C m in good agreement with the value $0.75 \ 10^{-31}$ C m measured by Page et al. (1984a). The temperature dependence of the dielectric susceptibility (per site volume) is presented in fig. 24, where the dashed curve corresponds to eq. (231) with the mean field $T_{\rm C}({\rm MFA}) = 1.91$ K. The mean field model cannot account for the cusp in $\chi_{\rm E}$ near the real critical temperature, due to the competing effects of short- and long-range interactions. Much better results in the description of the experimental data (the solid curve in fig. 24) were obtained by Page et al. (1984a) with the correlated-effective field model introduced by Lines (1974).

A distinctive type of critical behaviour of the dielectric susceptibility was observed by Page et al. (1984b) at the structural phase transitions in the DyVO₄ and DyAsO₄ Jahn– Teller ferroelastics. The z-component of the electric field transforms according to the same irreducible representation of the point D_{2d} symmetry group at Dy sites as does the spontaneous deformation $e(B_{1g})$ in the basal plane of the lattice. The dielectric and elastic responses of the crystals are completely separated due to different bulk symmetries. The electric susceptibility does not diverge but shows a peak at the transition temperature T_D corresponding to the antiparallel ordering of the electric dipole moments at the two Dy sites in the unit cell. An interaction of the two lowest Kramers doublets of a Dy ion with the electric field can be written just as in the case of a non-Kramers doublet and the effective dipole moments have been found to be $\gamma = 15$ and 4.2 in units of 10^{-31} C m for DyVO₄ and DyAsO₄, respectively (Page et al. 1984b). It should be noted that the formal estimate of the contribution of the electric dipolar interaction as γ^2/r^3 to the total interaction energy of the two lanthanide ions is incorrect though it gives values comparable in order of magnitude to $k_{\rm B}T_{\rm D}$, because the effective dipole moments $D^{(d)}$ only are to be considered in such calculations.

The problem of the nature of the electronic multipole ordering is especially interesting for some praseodymium hexagonal compounds with the doublet ground state E' of the Pr^{3+} ion in the crystal field of C_{3h} symmetry (chlorides, bromides, hydroxides, trifluoromethane sulfonates, ethylsulfates). In the effective $S = \frac{1}{2}$ formalism, neglecting hyperfine interactions, the single-ion Hamiltonian can be written as follows:

$$\mathcal{H}_{S} = g_{\parallel} \mu_{\mathrm{B}} H_{z} S_{z} + \gamma (E_{x} S_{x} + E_{y} S_{y}). \tag{232}$$

The salts mentioned above have $g_{\parallel} < 2$, and the effective electric dipole moments determined from the electric susceptibility measurements are by an order of magnitude larger than the magnetic dipole moments ($\gamma = 6.6$ (PrCl₃), 5.6 (PrBr₃), 3.2 (Pr(OH)₃), 2.3 (PrTFMS), 7.8 (PrES) in units of 10⁻³¹ Cm) (Harrison et al. 1976, Taylor et al. 1977, Folinsbee et al. 1977a,b, Fillion et al. 1980, Petasis et al. 1993). The interactions between the nearest Pr ions on the chains along the three-fold symmetry axis are dominant and are nearly of the ideal XY form given in eq. (125) with the interaction parameters from table 11. The magnetic interactions cannot be responsible for the XY-coupling, and no magnetic ordering was detected. Measurements of the dielectric susceptibility as well as of the specific heat temperature dependences indicated the characteristic features of onedimensional antiferroelectric ordering (the broad maxima), and some strong anomalies at lower temperatures were observed which could be identified with the structural 3D phase transitions due to weak interchain Jahn-Teller interactions (the transition temperatures are presented in table 22, only in the PrES no long-range order was found up to 0.06 K). In the x-y plane the dielectric susceptibility has the Curie-law (T^{-1}) behaviour at higher temperatures and is saturated as $T \rightarrow 0$. The symmetry of the low-temperature phase has not been definitely established as yet, and it would appear useful to conduct a theoretical investigation of the possible dimerization of the Pr ions involved, due to transition into an improper antiferroelectric phase with the cell doubling along the c-axis (Morra et al. 1983).

4.4. Magnetoelastic phenomena

The general theory of quasistatic magnetoelastic properties of the lanthanide compounds has been given in sect. 2 of this chapter. It involves a wide variety of possible types of low temperature behaviour and magnetic field effects on the lattice structure and elastic constants which depend on the energy spectra of the lanthanide ions in the crystal field and the relative strength of the one- and two-particle coupling with the lattice strains. It is evident that the peculiarities of the magnetoelastic properties should appear near the critical and multicritical temperatures. The most complicated behaviour might be assumed in crystals containing several magnetically inequivalent lanthanide ions in the unit cell [for example, Wolf and Huan (1988) discussed a large amount of magnetoelastic effects including the strain-induced magnetization in the DyAlG antiferromagnet with the multicomponent order parameter], and in crystals with competitive magnetic and electric multipole interactions undergoing structural phase transitions. In the latter case there occur structural domains and because of their reorientation due to the external field it is not easy to distinguish the proper magnetic field effects on the unit cell dimensions (Vekhter et al. 1986).

The mutual suppression of the structural and magnetic ordering determines the anomalous temperature behaviour of the forced magnetostriction in crystals exhibiting the cooperative Jahn-Teller effect (Kazei and Sokolov 1986). The regeneration of the undistorted phase at $T < T_D$ in an external magnetic field was observed in many Jahn-Teller systems. In particular, the spontaneous orthorhombic strain of the order of 6×10^{-3} disappears at 1.4 K in the magnetic fields $H > H_{\rm C} = 5.4$ kOe parallel to the c-axis in the TmVO₄ ferroelastic, and the corresponding value of $H_{\rm C}$ is equal to 21.3 kOe in TmAsO₄ (Bleaney et al. 1983b). Becker (1976) obtained different signs of the derivatives of the e_{xy} strain along the external magnetic field $H_0 \parallel [110]$ at $T > T_D$ and $T < T_D$ in TmAsO₄ with the method of linear optical birefringence. The magnetic field of $\sim 40 \text{ kOe}$ in the ac-plane at 45° to the axes, destroys the spontaneous crystallographic distortion in the two-sublattice antiferrodistortive $KDy(MoO_4)_2$ Jahn–Teller system at 4.2 K (Leask et al. 1981). The magnetic field effects on the elastic constants of the lanthanide compounds exhibiting the Jahn-Teller transitions were described by Melcher (1976). The peculiarities of the temperature behaviour of the magnetization of crystals with the cooperative Jahn-Teller effect (DyVO₄, TbVO₄) above and below $T_{\rm D}$ were investigated by Vekhter et al. (1988).

Spontaneous magnetoelastic effects in the lanthanide compounds induced by internal magnetic fields are usually relatively small. The forced magnetostriction and magnetoacoustic phenomena are much easier to study at low temperatures in applied fields of several Tesla. As a rule, in the lanthanide ferro- and antiferromagnets the magnitude of parastriction is determined similarly as in the VV paramagnets (see sect. 3.2), by the single-ion mechanism of magnetoelastic coupling. Only in special cases, when the single-ion mechanism appears to be ineffective due to symmetry-forbidden virtual transitions between the ground and excited sublevels of the ground manifold, become the two-particle interactions of importance. Here we shall restrict ourselves to some examples representing the most general peculiarities of the magnetoelastic effects in the compounds of the Kramers and non-Kramers ions, and to demonstrating the possibilities of the microscopic theory in the interpretation of the experimental data.

The forced magnetostriction is determined by the differences between the symmetrized components of the deformation tensor when $H_0 \neq 0$ and $H_0=0$ (see eqs. 99, 109); in the

mean-field approximation (with n magnetically equivalent ions in a cell) these are given by:

$$e_{\lambda}(\Gamma_{i}^{j}) = -\sum_{k} S(\Gamma_{i}^{jk}) \left\{ \frac{n}{v} B_{\lambda}^{(r)}(\Gamma_{i}^{k}) : \left[\langle O(H) \rangle_{0} - \left\langle O(\Lambda_{0}^{(0)} M_{0}^{(0)}) \right\rangle_{0} \right] -\frac{1}{2} M_{0} \Lambda_{\lambda}^{(r)}(\Gamma_{i}^{k}) M_{0} + \frac{1}{2} M_{0}^{(0)} \Lambda_{\lambda}^{(r0)}(\Gamma_{i}^{k}) M_{0}^{(0)} \right\},$$
(233)

where $S(\Gamma_i^{jk})$ are the symmetrized components of the elastic compliance tensor (see table 12), and $\langle O_p^k(H) \rangle_0$ are the canonical averages of operators O_p^k for a single magnetic ion in the field $H = H_0 + \Lambda_0 M_0$. The magnetization M_0 is determined by eq. (106) when $H_0 > H_{0c}$ (see sect. 4.1); if $H_0 < H_{0c}$, then $M_0 = M_0^{(0)}$, and the spontaneous magnetization $M_0^{(0)}$ corresponds to the internal magnetic field $\Lambda_0^{(0)} M_0^{(0)}$.

A peculiarity of the two-particle mechanism of magnetoelastic coupling in dipolar ferromagnets should be noted here – the molecular field constants $\Lambda_0^{(0)}$ and their derivatives along the components of the deformation tensor, $\Lambda^{(r0)}$ (see eq. 110), in the ferromagnetic phase at $H_0 = 0$ are different from Λ_0 and $\Lambda^{(r)}$ in the paramagnetic phase, due to the development of a specific domain structure with the zero demagnetizing field at $T < T_c$.

At low temperatures, when only the ground state of the lanthanide ion in the crystal field is populated, the total magnetic moment of the ion is the sum of the induced (Van Vleck) moment and the intrinsic moment (the latter differs from zero only in the degenerate state). The contributions to the magnetostriction and the elastic constants due to changes in the intrinsic magnetic moment of the lanthanide ion with lattice strain can be written explicitly when considering the effective spin Hamiltonian. The latter contains a smaller number of independent parameters (constants of spin–phonon interaction) than the Hamiltonian of the electron–deformation interaction (18) and is more suitable in the description of experimental data.

Let the ground state of the lanthanide ion be the Kramers doublet (effective spin $S = \frac{1}{2}$). Then the spin Hamiltonian, linear in lattice strains, is given in eq. (116). In accordance with eq. (233) we obtain the parastriction due to the strain modulation of the doublet shift and splitting as follows

$$e_{\alpha\beta}(H_0,T) = S_{\alpha\beta\gamma\delta}(T) \left[\frac{n}{v} B_{\gamma\delta}(h) H_0 \tanh \frac{g\mu_{\rm B}H_0}{2k_{\rm B}T} + \frac{1}{2}\chi^{(0)}_{\rho\sigma\gamma\delta}H_{0\rho}H_{0\sigma} \right],$$
(234)

which may be rewritten in symmetrized form as

$$e_{\lambda}(\Gamma_i^j) = \sum_k S(\Gamma_i^{jk}|T) \left[\frac{n}{v} B_{\lambda}(\Gamma_i^k, \boldsymbol{h}) H_0 \tanh \frac{g\mu_{\rm B}H_0}{2k_{\rm B}T} + \frac{1}{2}\chi^{(0)}(\Gamma_i^k, \boldsymbol{h}) H_0^2 \right], \qquad (235)$$

where **h** is the magnetic field unit vector $(h_{\alpha} = H_{0\alpha}/H_0)$, $g = (g_{\alpha\beta}g_{\gamma\beta}h_{\alpha}h_{\gamma})^{1/2}$ is the effective g-factor, and

$$B_{\gamma\delta}(\boldsymbol{h}) = \frac{1}{2g} \mu_{\rm B} g_{\alpha\beta} G_{\rho\beta\gamma\delta} h_{\alpha} h_{\rho}, \qquad (236)$$

$$\chi^{(0)}_{\alpha\beta\gamma\delta} = -\frac{2n}{\nu} (g_{\rm J}\mu_{\rm B})^2 \sum_{pq} B^{(r)q}_{p,\gamma\delta} \left\{ \sum_{lm} \varepsilon_l^{-1} \varepsilon_m^{-1} [lm, \alpha\beta]_p^q - \sum_l \varepsilon_l^{-2} [l, \alpha\beta]_p^q \right\}.$$
(237)

Expression (237) has the same structure as the third-order correction to the ground-state energy, linear in each summand of the perturbation $J_{\alpha} + J_{\beta} + O_p^q$:

$$[lm, \alpha\beta]_{p}^{q} = \langle -|J_{\alpha}|l\rangle \langle l|J_{\beta}|m\rangle \langle m|O_{p}^{q}|+\rangle + \langle -|J_{\alpha}|l\rangle \langle l|O_{p}^{q}|m\rangle \langle m|J_{\beta}|+\rangle + \langle -|O_{p}^{q}|l\rangle \langle l|J_{\alpha}|m\rangle \langle m|J_{\beta}|+\rangle,$$
(238)

$$[l, \alpha\beta]_{p}^{q} = \langle -|O_{p}^{q}|-\rangle \langle -|J_{\alpha}|l\rangle \langle l|J_{\beta}|-\rangle + 2 \langle -|J_{\alpha}|-\rangle \operatorname{Re} \langle -|J_{\beta}|l\rangle \langle l|O_{p}^{q}|-\rangle +\operatorname{Re} \left[\langle -|O_{p}^{q}|l\rangle \langle l|J_{\alpha}|+\rangle \langle +|J_{\beta}|-\rangle + \langle -|J_{\alpha}|l\rangle \langle l|O_{p}^{q}|+\rangle \langle +|J_{\beta}|-\rangle \right],$$
(239)

where $|+\rangle$ and $|-\rangle$ are Kramers conjugated states of the ground doublet and $|l\rangle$ are the wave functions of the excited states with the energies ε_l .

Thus the relative change in sample dimensions along the unit vector n in the paramagnetic phase has the general form

$$\left(\frac{\Delta L}{L}\right)_{n} = A(\boldsymbol{n}, \boldsymbol{h}) H_{0}^{2} + B(\boldsymbol{n}, \boldsymbol{h}) H_{0} \tanh\left(\frac{g\mu_{B}H_{0}}{2k_{B}T}\right) + C(\boldsymbol{n}, \boldsymbol{h}) \tanh^{2}\left(\frac{g\mu_{B}H_{0}}{2k_{B}T}\right),$$
(240)

where A, B and C are linear combinations of the constants of electron-deformation couplings, spin-phonon couplings, and the strain derivatives of the two-particle interaction, respectively. In a weak magnetic field $(g\mu_BH_0 \ll k_BT)$ the parastriction is linear in H_0^2 . The relative significance of the different terms in eq. (240) varies with temperature and magnetic field.

Contributions to the elastic constants of the lanthanide compounds induced by the magnetic field may be considered in the same way by using eqs. (95) and (105). We only have to mention that the dependence of the acoustic wave velocities on the magnetic field is a consequence of the appearance of coupled electron-phonon excitations, carrying a magnetic moment. Magnetoacoustic vibrations are generated by an alternating magnetic field and can be detected by means of alternating magnetization, induced when the coupled vibrations reflect from the sample surface (Aukhadeev et al. 1987). Acoustic birefringence and the acoustic Faraday effect in lanthanide compounds in an external magnetic field were considered by Thalmeier and Fulde (1978).

Bumagina et al. (1981) and Krotov et al. (1982) used the general formula for the forced magnetostriction presented above, for the interpretation of the low-temperature measurements of the magnetoelastic effects in the crystals of the $LiRF_4$ fluorides. The

longitudinal magnetostriction of the LiRF₄ tetragonal lattice in an applied field $H_0(\theta, \phi)$ (the crystallographic coordinate system is used with the polar axis along the *c*-axis) according to eq. (111) equals (see table 8)

$$\left(\frac{\Delta L}{L}\right)_{\parallel} = \cos^2\theta \,e(\mathbf{A}_g^1) + \sin^2\theta \,e(\mathbf{A}_g^2) + \sin^2\theta \left[\cos 2\phi e(\mathbf{B}_g^1) + \sin 2\phi e(\mathbf{B}_g^2)\right] + \sin 2\theta \left[\cos\phi e_1(\mathbf{E}_g) + \sin\phi e_2(\mathbf{E}_g)\right].$$
(241)

All the single-ion parameters necessary for calculating the dependence of magnetostriction on temperature, magnitude, and orientation of the magnetic field, were found in the framework of the exchange charge model. Some of them were confirmed by investigations of the optical and EPR spectra of lanthanide impurity ions in uniaxially stressed LiRF₄ samples (R=Tm, Y, Lu). To specify the parameters of exchange interactions they were taken into account only for the nearest neighbours (v = 1-4) and it was assumed that the exchange integrals $A_{\alpha\beta}(v)$ depended only on the distance $r = (\frac{1}{4}a^2 + \frac{1}{16}c^2)^{1/2}$ (*a*, *c* are the lattice constants) between the R-ions. According to eqs. (72) and (76) the molecular field constants in paramagnetic and ferromagnetic phases (at $H_0 > H_{0c}$) equal

$$\Lambda_{0,\alpha\beta} = \frac{v}{2} \left[Q_{\alpha\beta}(R_1, R_1) + Q_{\alpha\beta}(R_1, R_2) - (g_J \mu_B)^{-2} \sum_{\nu} A_{\alpha\beta}(\nu) \right] - D_{\alpha\beta}.$$
 (242)

The variations of the molecular field constants, due to the lattice deformation (eq. 80), are determined by changes of the dipolar, exchange, and demagnetizing fields. Within the framework of the model introduced above, the exchange field is modulated only by the totally symmetrical (A_g^k) lattice deformations. The contribution of the dipolar field into $A^{(e)}$ is $\frac{v}{2} \sum_{R'} Q_{\alpha\beta,\gamma\delta}(R, R')$, where the values of $Q_{\alpha\beta,\gamma\delta}(\lambda,\lambda')$ are determined by eq. (64). The exponential dependence of exchange integrals on r can be assumed for estimates of the exchange field contributions: $A_{\alpha\beta}(v) = A_{\alpha\beta} \exp(-r/p_0)$. The contribution of the demagnetizing field is $\Lambda_{D\alpha\beta,\gamma\delta}^{(e)} = D_{\alpha\beta}\delta_{\gamma\delta} - D_{\alpha\beta,\gamma\delta}$, where the first and second terms correspond to the change of volume and shape of the sample, respectively. An internal deformation affects the dipolar field only at B_g and E_g deformations. Numerical calculations of the lattice sums result in the following values of the components of the tensor (110), which determine the changes of the internal magnetic field in a spherical-shaped sample at fully symmetrical deformations:

$$A_{xx}^{(r)}(A_{g}^{1}) = -4.884 + \frac{\alpha}{p_{0}}A_{xx} + \frac{4}{5}\pi, \qquad A_{xx}^{(r)}(A_{g}^{2}) = -5.691 + \frac{\beta}{p_{0}}A_{xx} + \frac{16}{5}\pi,$$

$$A_{zz}^{(r)}(A_{g}^{1}) = -3.80 + \frac{\alpha}{p_{0}}A_{zz} + \frac{12}{5}\pi, \qquad A_{zz}^{(r)}(A_{g}^{2}) = -13.75 + \frac{\beta}{p_{0}}A_{zz} + \frac{8}{5}\pi,$$
(243)

where $\alpha = c^2 v/8rg_J^2 \mu_B^2$, $\beta = a^2 v/2rg_J^2 \mu_B^2$. The last terms in eqs. (243) are shape-dependent; in particular, for samples in the form of a long thin cylinder these terms are replaced

NONMETALLIC LANTHANIDE COMPOUNDS

	Constants of spin-	ns in LiRF ₄ crystal	S		
$G_{ij}(\Gamma_k)$	Er ³⁺	Dy ³⁺	$G_{ij}(\Gamma_k)$	 Er ³⁺	Dy ³⁺
$\overline{G_{11}(\Gamma_1)}$	-25.5		$G_{12}(\Gamma_1)$	1.8	
$G'_{21}(\Gamma_1)$	8.4		$G'_{22}(\Gamma_1)$	-1.2	
$G_{11}(\Gamma_2)$	-61.4	-145	$G_{12}(\Gamma_2)$	-49.8	889
$G_{21}(\Gamma_2)$	-28.9	429	$G_{22}(\Gamma_2)$	-86	-713
$G(\Gamma_{34})$	-23.2		$G'(\Gamma_{34})$	-46.6	
$G''(\Gamma_{34})$	30.2				

Table 25 rts of spin phonon interaction of \mathbf{Fr}^{3+} and \mathbf{Du}^{3+} ions in LiPE

by 2π and 4π , 0 and 0 in the first and second lines, respectively. In weak magnetic fields $H_0 < H_{0c}$ at $T < T_C$ the values of $\Lambda_{\lambda,\alpha\beta}^{(r0)}(\Gamma_i^k)$ are obtained from $\Lambda_{\lambda,\alpha\beta}^{(r)}(\Gamma_i^k)$ by assuming that the contributions of the demagnetizing field equal zero. As a result, the macroscopic forced magnetostriction, completely determined by the sample shape in accordance with eq. (233), appears in the region of the existence of the domain structure ($H_0 < H_{0c}$) though the internal field and magnetization do not depend on H_0 . This phenomenon has been observed, in particular, in the measurements of magnetostriction in the LiTbF₄ samples.

The spin Hamiltonian of the Er^{3+} and Dy^{3+} ions in the LiRF₄ crystals is given by formula (118) with the Zeeman term in the form of eq. (119) and with $G''_{2j}(\Gamma_1)=0$. The constants of spin-phonon interaction, calculated with the parameters of electrondeformation interaction from table 10, are given in table 25 (some of these constants were measured in EPR experiments on the uniaxially stressed LiTmF₄ crystals activated by the Er^{3+} and Dy^{3+} ions). In this case parameters of the magnetostriction $B_{\lambda}(\Gamma_i^k, h)$ in eq. (235) can be written as follows

$$B(A_{g}^{j}) = \frac{\mu_{B}}{2g} \left[g_{\parallel} G_{1j}(\Gamma_{1}) \cos^{2} \theta + g_{\perp} G_{2j}^{\prime}(\Gamma_{1}) \sin^{2} \theta \right],$$
(244)

$$B(B_{g}^{j}) = \frac{g_{\perp} \mu_{B}}{2g} \left[G_{1j}(\Gamma_{2}) \cos 2\phi + G_{2j}(\Gamma_{2}) \sin 2\phi \right] \sin^{2} \theta,$$
(245)

$$B_{1}(E_{g}) = \frac{\mu_{B}}{4g} \left\{ \left[g_{\parallel} G(\Gamma_{34}) + g_{\perp} G'(\Gamma_{34}) \right] \cos \phi - g_{\perp} G''(\Gamma_{34}) \sin \phi \right\} \sin 2\theta,$$
(246)

$$B_{2}(E_{g}) = \frac{\mu_{B}}{4g} \left\{ \left[g_{\parallel} G(\Gamma_{34}) + g_{\perp} G'(\Gamma_{34}) \right] \sin \phi + g_{\perp} G''(\Gamma_{34}) \cos \phi \right\} \sin 2\theta,$$
(247)

where $g = (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2}$. Similar dependences on the magnetic field angular variables can be easily obtained for the parameters of the VV magnetostriction $\chi^{(0)}(\Gamma_i^k, h)$. The results of calculations with the data of tables 10, 12, and 25, brought out evidence of dominant single ion magnetoelastic effects in the LiErF₄ crystal in accordance with the experimental data and made it possible to predict a giant parastriction in the [110] direction in LiDyF₄, which was confirmed in later experiments. Abdulsabirov et al.

(1995) used the Tm³⁺ impurity ions to probe the internal lattice structure of the LiDyF₄ crystal. They found the maximum splitting of the optical transition between the ground singlet and excited doublet (${}^{3}F_{2}$, Γ_{34}) to be 4 cm⁻¹ in the magnetic field, 16 kOe along the [110] direction in the lattice basis plane at 4.2 K. Such a splitting corresponds to the giant deformation of about 1.5×10^{-3} and it may be induced by an uniaxial stress of an order of 100 MPa. It should be noted that in the same experimental conditions, the splitting of this transition of the Tm³⁺ impurity ions in the nonmagnetic LiYF₄ crystal does not exceed 0.02 cm^{-1} . The relative significance of different terms in the LiErF₄ macroscopic parastriction (240) in the range of low field intensities may be seen from the corresponding terms in coefficients (146) given below:

$$\alpha(T, \mathbf{n} = \mathbf{h} = [001]) = \left(-\frac{1.69}{T} + 0.16 + \frac{0.086}{T^2}\right) \times 10^{-7} \,\mathrm{kOe^{-2}},$$

$$\alpha(T, \mathbf{n} = \mathbf{h} = [100]) = \left(-\frac{22.8}{T} + 0.87 + \frac{9.8}{T^2}\right) \times 10^{-7} \,\mathrm{kOe^{-2}}.$$

The coefficients of the longitudinal magnetostriction measured by Bumagina et al. (1981) at helium temperature are equal to

$$\alpha([001]) = -0.24(-0.22) \times 10^{-7} \,\mathrm{kOe^{-2}}, \qquad \alpha([100]) = -4.0(-3.8) \times 10^{-7} \,\mathrm{kOe^{-2}}$$

(calculated values in parentheses). The sample dimensions changed approximately linearly in the applied magnetic field in the fields $H_0 > 10$ kOe. No saturation of the parastriction was observed up to 30 kOe, in this field along the [110] direction at 4.2 K $\Delta L/L = -2 \times 10^{-5}$. In spite of the fact that the exchange charge model of the crystal field and the model of lattice dynamics which have been used are approximate in nature, the theory presented in sect. 2.5 predicts correctly the sign and magnitude of the magnetostriction for an arbitrary orientation of the external magnetic field.

Al'tshuler et al. (1984) observed clear anomalies, similar to those shown in fig. 25, in the absence of applied field in the temperature dependence of the propagation time of 13 MHz transverse acoustic waves along the *c*-axis through LiDyF_4 and LiErF_4 samples at the Néel temperature. The relative change of the propagation time,

$$\frac{\Delta t(T)}{t} = \frac{t(T) - t(3 \mathrm{K})}{t(3 \mathrm{K})} = \frac{\Delta L(T)}{L} - \frac{\Delta v_{\mathrm{t}}(T)}{v_{\mathrm{t}}}$$

had a maximum at T_N with an abrupt decrease when the temperature fell below T_N due to the combined effect of the spontaneous magnetostriction and the change in the elastic constant C_{44} ($v_t^2 = C_{44}/d$). The magnitude of the drop in $\Delta t/t$ at temperatures close to 0.1 K reached the value of 3×10^{-4} in LiDyF₄ and was in agreement with the theoretical estimates based on a single-ion mechanism of the electron-deformation interaction.

The anisotropy (as well as temperature and magnetic field dependences) of the induced magnetostriction in LiHoF₄ and $Tb_2Ti_2O_7$ crystals, measured by Al'tshuler et al. (1984)



Fig. 25. Temperature dependence of the velocity of transverse acoustic waves $(H_0 || q || [001])$ in LiHoF₄ Ising ferromagnet. The data of measurements (Al'tshuler et al. 1984) are shown by open $(H_0 = 0)$ and solid $(H_0 = 3 \text{ kOe})$ circles, the curve represents the results of calculations.

and Aleksandrov et al. (1985), respectively, with maximum values of the order of 10^{-4} in magnetic fields of 30–50 kOe at liquid helium temperatures, is in compliance with the dominant role of the single ion electron–lattice interaction, too. A sufficiently small energy gap between the ground and excited sublevels of the lanthanide ions is a common property of all compounds mentioned above.

Quite different magnetoelastic effects were observed by Krotov et al. (1982) and Aukhadeev et al. (1983) in the LiTbF₄ Ising ferromagnet, where the two lower singlets of the Γ_2 symmetry, well separated from the other sublevels of the ground multiplet, can interact through fully symmetrical strains only. The magnetic parameters of this crystal are given in table 11 and the magnetic properties were discussed in the preceding section. In an applied field $H_0 \parallel [001]$ the splitting of the quasidoublet equals $\delta = [\delta_0^2 + (g_{\parallel} \mu_{\rm B} H)^2]^{1/2}$, where $H = H_0 + \Lambda_0 M_0$ is the internal magnetic field in the paramagnetic phase and in the ordered phase when $H_0 > D_{zz} M_0^{(0)} = H_{0c}$. The magnetization satisfies the equation

$$M_0 = \frac{(g_{\parallel} \mu_{\rm B})^2}{v\delta} H \tanh \frac{\delta}{2k_{\rm B}T},$$
(248)

which, in the paramagnetic phase, gives for small H_0 the simple expression

$$M_0(T > T_C) = \frac{b}{1 - \Lambda_0 b} H_0 + O(H_0^3),$$
(249)

where

$$b = \frac{\tanh\left(\delta_0/2k_{\rm B}T\right)}{\Lambda_0^{(0)}\tanh\left(\delta_0/2k_{\rm B}T_{\rm C}\right)}$$

The spontaneous magnetization $M_0^{(0)}$ in the domains can also be obtained from eq. (248), but with the substitution of $\Lambda_0^{(0)}M_0^{(0)}$ for *H*. The molecular field constant in the domains

with zero demagnetizing field $\Lambda_0^{(0)} = 4.325$ is connected with the Curie temperature by the simple relation

$$\Lambda_0^{(0)} = \left(\frac{(g_{\parallel}\mu_{\rm B})^2}{\nu\delta_0} \tanh\frac{\delta_0}{2k_{\rm B}T_{\rm C}}\right)^{-1}.$$
(250)

The longitudinal induced magnetostriction can be written as a function of temperature and external magnetic field in accordance with eqs. (233) and (241):

$$\frac{\Delta L}{L}([001]) = AM_0^2 + BH^2 + CM_0H + F\left(\frac{M_0}{H} - b\right) - \theta(T_{\rm C} - T) \left[(A^{(0)} + BA_0^{(0)2} + CA_0^{(0)})M_0^{(0)2} + F\left(\frac{1}{A_0^{(0)}} - b\right) \right],$$
(251)

where $\theta(x)$ is a unit step-function; constants *B*, *C*, and *F* define the corrections to the energies of the ground quasidoublet states due to the electron-deformation interaction linear in the parameters $B_p^{(r)q}(A_g^i)$ which are given in table 10. The contributions due to the two-particle magnetoelastic interactions are specified by the constants (see eq. 243)

$$A = \frac{1}{2} \left[S(A_g^{11}) \Lambda_{zz}^{(r)}(A_g^1) + S(A_g^{12}) \Lambda_{zz}^{(r)}(A_g^2) \right]$$
(252)

and $A^{(0)}$; $A^{(0)}$ results from A upon the substitution of $\Lambda_{zz}^{(r0)}(A_g^i)$ for $\Lambda_{zz}^{(r)}(A_g^i)$. In the paramagnetic phase the induced magnetostriction can be presented by the formula (146) linear in H_0^2 with the proportionality coefficient

$$\alpha(T > T_{\rm C}, \ [001]) = (1 - \Lambda_0 b)^{-2} \left\{ A b^2 + B + C b + \frac{b}{2} F \left(\frac{g_{||} \mu_{\rm B}}{\delta_0} \right)^2 \left[\frac{\delta_0}{k_{\rm B} T \sinh(\delta_0 / k_{\rm B} T)} - 1 \right] \right\}.$$

In a transverse magnetic field $H_0 \perp [001]$ the field and temperature dependences of the induced longitudinal magnetostriction in the LiTbF₄ dipolar ferromagnet in accordance with eqs. (233), (235), and (241) are described by the expression

$$\frac{\Delta L}{L}(\boldsymbol{H}_0 \perp c) = \left[\alpha_1(\phi) + \alpha_2(\phi) \frac{\delta_0}{\delta_\perp} \tanh \frac{\delta_\perp}{2k_{\rm B}T} \right] H_0^2, \tag{253}$$

where the splitting of the ground quasidoublet equals

$$\delta_{\perp} = \left[\delta_0^2 + \left(g_{\parallel}\mu_{\rm B}\Lambda_0^{(0)}M_0^{(0)}\right)^2\right]^{1/2},\tag{254}$$

and $\alpha_i(\varphi)$ are the functions of the angle φ which determines the orientation of the magnetic field H_0 in the basal lattice plane. In this case the crystal has only an induced



Fig. 26. Forced magnetostriction in the LiTbF₄ Ising ferromagnet ($T_c = 2.885$ K) in the longitudinal field $H_0 \parallel [001]$. The solid curves represent experimental data obtained at 4.2 K (1) and 1.6 K (2). The dashed curves denote the results of calculations based on eq. (251) with the parameters $A = 91.4 \times 10^{-7}$ kOe⁻²; $A^{(0)} = 74.8 \times 10^{-7}$ kOe⁻²; $B = -5.8 \times 10^{-10}$ kOe⁻²; $C = 1.2 \times 10^{-7}$ kOe⁻²; $F = -62 \times 10^{-7}$.

magnetic moment in the field direction and the single-ion mechanism of magnetoelastic interaction prevails above and below the transition point. The interaction of the Tb³⁺ ions with the axial deformations of the B_g symmetry contributes mainly to the coefficients $\alpha_i(\varphi)$ in eq. (253). The change in the initial splitting δ_0 due to the VV magnetization is very small and it has been neglected when writing down eq. (253). Equations (248) and (250) yield

$$\frac{\delta_0}{\delta_{\perp}} \tanh \frac{\delta_{\perp}}{2k_{\rm B}T} = \tanh \frac{\delta_0}{2k_{\rm B}T_{\rm C}} \propto \frac{1}{\Lambda_0^{(0)}},$$

and at temperatures below $T_{\rm C}$ the induced magnetostriction in the transverse field remains temperature independent.

The results of the calculations are compared with the data of measurements in figs. 26–28. The temperature dependence of an induced magnetostriction exhibits clearly defined features at the ordering point. The qualitative difference in the temperature and field dependences of magnetostriction above and below the Curie point suggests that the two-particle mechanism of magnetoelastic interactions is the dominant mechanism in this compound. In a strong longitudinal magnetic field the magnetostriction reaches saturation both above and below the transition point (fig. 26) presumably because of the saturation of the magnetization. The difference between the spontaneous magnetization $M_0^{(0)}$ and the magnetization M_0 in the external field $H_0 > H_{0c}$ tends towards zero as $T \rightarrow 0$ and the field-induced lattice deformation, proportional to $M_0^{(0)2}$, also decreases (fig. 27). It should



Fig. 27. Temperature dependence of the induced magnetostriction in LiTbF₄ along a field $H_0 \parallel [001]$. The dashed curve represents the calculated values of magnetostriction in the 22.5 kOe field.

Fig. 28. Temperature dependence of the induced magnetostriction in LiTbF₄ along the 20 kOe field $H_0 \perp [001]$. The dashed curve represents the calculated values of magnetostriction obtained with eq. (253).

be noted that at $T < T_C$ (see curve 2 in fig. 26) the induced magnetostriction is entirely shape dependent in the range $0 < H_0 < H_{0c}$. The magnetostriction in transverse field (see fig. 28) may be compared with the parastriction of the LiTmF₄ VV paramagnet considered in sect. 3.2. Since the energy of the excited states of the Tb³⁺ ion is relatively high,



Fig. 29. Temperature dependence of the velocity of the transverse sound in LiTbF₄ along the magnetic field $H_0 \parallel [001]$. (a) experimental data; (b) results of calculations (Aukhadeev et al. 1983). A, $H_0 = 0$; B, 3 kOe; C, 6 kOe; D, 9 kOe; E, 30 kOe.

relatively high, the absolute striction of $LiTbF_4$ in comparable fields is considerably smaller than that of $LiTmF_4$. In contrast with the magnetostriction of $LiTmF_4$, the lattice deformation induced in the paramagnetic phase of the $LiTbF_4$ ferromagnet changes with the temperature because of the redistribution of the population of the lower singlets.

A remarkable effect of strain modulation of the exchange interactions on the elastic properties of the LiTbF₄ ferromagnet (see eq. 105) was observed by Aukhadeev et al. (1983). For example, below $T_{\rm C}$ the velocity v of purely transverse ultrasonic waves of frequency 13 MHz with the wave vector along the [001] direction of the crystal increases sharply, as is evident in fig. 29a which shows the relative variations

$$\frac{\Delta v}{v} = \frac{v(T, H_0) - v(4.2 \,\mathrm{K}, H_0)}{v(4.2 \,\mathrm{K}, H_0)}$$

An external magnetic field $H_0 \parallel [001]$ leads to a suppression of this effect due to the saturation of the magnetization. The results of calculations performed within the framework of the theory presented in sect. 2.5 accord to the experimental data as may be seen in fig. 29b.

4.5. Magnetic resonance

4.5.1. Magnetic resonance spectra

In the presence of strong internal fields NMR in a ferromagnetic phase of the examined compounds can be observed even without an external field. The resonance frequency of a proton located at the j-th position in a lattice is equal to

$$\nu_{j}(0) = \frac{\gamma}{2\pi} \mu_{z}^{0} \left[(\Sigma_{jx})^{2} + (\Sigma_{jy})^{2} + (\Sigma_{jz} + \frac{4}{3}\pi n_{0})^{2} \right]^{1/2}.$$
(255)

These frequencies are as follows for protons of different groups in TbES and DyES:



Fig. 30. Proton resonance frequencies in the TbES ferromagnetic crystal and their dependence on the external magnetic field.

Proton position	HIA	H1B	H2	H4	H5A	H5B
$\overline{\nu(0)}$ in TbES, MHz	0.135	0.147	2.47	8.42	15.04	21.3
v(0) in DyES, MHz	0.097	0.089	1.65	5.54	9.89	14.0

If the applied field is directed along the *c*-axis of a sphere-shaped axial ferromagnetic crystal, and its value does not exceed the Lorentz field $H_{\rm L}$, the resonance frequency $v_j(H_{0z} < H_{\rm L})$ does not differ from eq. (255). At $H_{0z} > H_{\rm L}$, NMR frequencies are calculated according to the formula

$$\nu_{j}(H_{0z} > H_{L}) = \frac{\gamma}{2\pi} \left[\mu_{z}^{2} \left[(\Sigma_{jx})^{2} + (\Sigma_{jy})^{2} + (\Sigma_{jz})^{2} \right] + 2\mu_{z}H_{0z}\Sigma_{jz} + H_{0z}^{2} \right]^{1/2}.$$
 (256)

The results of such calculations for the NMR in TbES are shown in fig. 30 by solid lines. This figure is also suitable for finding resonance frequencies of protons in the paramagnetic phase of TbES, that is, at temperatures above 0.24 K, if the Tb³⁺ ion polarization $P_0 = \tanh(\delta/2k_BT)$ is close to unity.

A peculiar picture of the inhomogeneous internal field structure in ferromagnetic crystals emerges when one studies the effective fields on different nuclei belonging to the same group. H5A nuclei in ethylsulfates can serve as an example. There are six different H5A positions corresponding to the apices of a triangular prism, whose center is occupied by a rare-earth ion. The directions of the internal fields are different for all six H5A protons. Two such groups of six protons belonging to the same unit cell are drawn separately in fig. 31. If the applied field is directed along the *c*-axis (or is absent), the pattern of effective field orientations is symmetrical: for six nuclei these fields are connected with each other by rotation C_6 around the *c*-axis. As a result, one NMR line will be observed. If the applied field deviates from the *c*-axis, the symmetry is broken and several NMR lines appear instead of a solitary one. In fig. 32 the molecular fields



Fig. 31. Molecular field directions at H5A protons in the TbES and DyES ferromagnetic crystals.

Fig. 32. Molecular field directions at H5A protons in the TbES and DyES ferromagnetic crystals projected on the a-b plane.

 $H_{Mj}(\theta_{Mj}, \phi_{Mj})$ on the H5A protons and an applied field $H_0(\theta, \phi)$ are shown by their projections on the *ab* plane; the *x*-axis is directed along the crystallographic *a*-axis. The absolute value of the effective field on the *j*-th proton is determined for a small inclination angle θ by the following expression

$$H_j \approx H + \left(\frac{H_0 H_{\mathrm{M}\perp}}{H}\right) \theta \cos(\phi - \phi_{\mathrm{M}j}),$$
(257)

where H is the value of the effective field at $\theta = 0$, and $H_{M\perp} = |H_{Mj}| \sin \theta_{Mj}$ is the transverse component of the field H_{Mj} which is the same for all j's.

We shall now list some experimental results concerning proton resonance spectra in TbES and DyES crystals (Aminov et al. 1985, 1988). The dependence of the spin echo amplitude on an external field $H_0 || c$ is shown in fig. 33. Due to a number of reasons (different orientation of a field H_1 relative to H_j on protons of different groups, different



Fig. 33. Proton magnetic resonance spectra in (a) TbES and (b) DyES crystals in the field $H_0||c$ at 13.4 MHz and 0.3 K; "extra" lines in the spectra are due to protons in the materials of the RF coil and to the liquid helium-3 in the mixing chamber of the ³He– ⁴He refrigerator.

relaxation times T_1 and T_2) the peak amplitudes in fig. 33 do not correspond to the true intensities of NMR spectrum lines; however the locations of these peaks on the H_0 scale are in fair agreement with the calculated resonance fields of protons belonging to different groups (see fig. 30). There are two additional peaks in the experimental spectra: one of them (¹H) is due to the protons in the materials of the NMR pick up device, the other is due to liquid ³He in the mixing chamber of the ³He–⁴He refrigerator.

The experimental spectra, as mentioned above, can be distorted due to the inaccurate settlement of crystals in the magnetic field H_0 : splittings and additional line shifts appear when the crystal *c*-axis deviates from the direction of the field H_0 . Therefore it will be most proper to compare the measured and calculated NMR frequencies in ferromagnetic crystals in the absence of an external field. The resonance of the H5A protons in both crystals have been observed; at temperatures $T < 0.8 T_{\rm C}$ the frequencies of these resonances,

$$v_{\rm H5A}^{(0)} = 15.2 \,\text{MHz} \text{ in TbES}, \quad v_{\rm H5A}^{(0)} = 10.0 \,\text{MHz} \text{ in DyES},$$
 (258)

exceed the calculated values by only 1%. Such good agreement confirms the ideas on static magnetic fields in the crystals in question.

Crystal	m_0^{\max}		¹⁹ F					⁷ Li		
	$(Oe cm^3/g)$	σ_{xx}	σ_{yy}	σ_{zz}	ζ	$(\sigma_{zx} + \sigma_{yz})^{1/2}$	σ_{xx}	σ_{yy}	σ_{zz}	ζ
LiTbF₄	205	-35.81	-7.75	-13.20	-18.92	52.0	4.4	4.4	-8.88	0
		(0.82)	(0.46)	(0.12)	(0.94)	(0.5)	(1)	(1)	(0.18)	(1)
LiHoF₄	158	-32.26	0.81	-6.00	-12.48	66	5.0	5.0	-10.0	0
		(0.40)	(0.24)	(0.09)	(0.48)	(1)	(1)	(1)	(0.6)	(1)

Table 26 ¹⁹F and ⁷Li NMR shift components in LiTbF₄ and LiHoF₄ in g/cm³ (Hansen and Nevald 1977, Nevald and Hansen 1978)

Measurement errors are given in parentheses.

The NMR spectra of ¹⁹F and ⁷Li in LiTbF₄ and LiHoF₄ were investigated by Hansen and Nevald (1977) and Nevald and Hansen (1978). For a more appropriate interpretation of measurements in wide ranges of temperatures and magnetic fields, the authors introduced a tensor σ of the NMR shift by defining the local magnetic field on the *j*th type nuclei as

$$\boldsymbol{H}_{i} = \boldsymbol{H}_{0} + \boldsymbol{\sigma}_{i} \, \boldsymbol{m}_{0}, \tag{259}$$

where m_0 is the crystal magnetization per gram, and the NMR shift tensor in a spherical sample has the form

$$\boldsymbol{\sigma}_{j} = \boldsymbol{\zeta}_{j} + \boldsymbol{\varepsilon}_{j} + \boldsymbol{\delta}_{j}, \tag{260}$$

where the scalar ζ_j and the tensor ε_j correspond to isotropic and anisotropic transferred hyperfine interactions and δ_j to the magnetic dipole–dipole interaction of the chosen nucleus with the surrounding lanthanide ions. The following conclusions may be drawn from the results of measurements (shown in table 26). The ⁷Li nuclear moments are coupled to lanthanide ions only through dipole–dipole interactions (distances ≥ 3.68 Å) while the overlapping of electron orbits plays an important role in the interaction of lanthanide ions with the nuclear moments of ¹⁹F (distances ≥ 2.25 Å). The isotropic part of the transferred hyperfine interaction "lanthanide ion–F" does not depend on temperature (1.3–300 K), magnetic field (up to 40 kOe), and is negative in sign; no anisotropic transferred hyperfine interaction is revealed.

Using the data of table 26, one can estimate the molecular fields in ferromagnetic crystals:

$$H_{M\perp} = (H_{Mx}^2 + H_{My}^2)^{1/2} = m_0^{\max} (\sigma_{zx}^2 + \sigma_{yz}^2)^{1/2}, \qquad H_{Mz} = m_0^{\max} \sigma_{zz}, \tag{261}$$

and predict the NMR frequencies of fluorine and lithium in these fields. However, NMR of the ¹⁹F and ⁷Li nuclei in the internal fields of ferromagnets LiTbF₄ and LiHoF₄ has

not been observed as yet. An attempt to observe the spin echo in a LiTbF₄ single crystal failed because of the strong effects of magnetostriction (Al'tshuler et al. 1975).

The EPR spectra of lanthanide ions in LiTbF₄ and LiHoF₄ were investigated in both paramagnetic and ferromagnetic states (Magarino et al. 1978, 1980, de Groot et al. 1981, Janssen et al. 1983, 1985). The main difficulty was a strong broadening of the resonance lines due to the excessive dipolar coupling between ions. To overcome this difficulty experiments were carried out in conditions of high polarization, by use of strong magnetic fields (up to 70 kOe) and, correspondingly, of high resonance frequencies (up to 1600 GHz). The most notable result of these experiments seems to be the fact that spin excitations at temperatures both above and below the Curie point are mainly one-particle excitations as in an ordinary EPR. The known structure (from other experiments) of the lower energy levels of Tb³⁺ and Ho³⁺ ions in the crystal field was confirmed.

A series of EPR measurements (along with optical and magnetic susceptibility studies) in lanthanide nicotinate dihydrates (RND) was carried out by Baker et al. (1986a,b, 1987, 1988, 1991a,b). These compounds with stoichiometric formula $[R(C_5H_4NCO_2)_3(H_2O)_2]_2$ have a dimeric molecular crystal structure with space group P2₁/c. Two lanthanide ions in a dimeric pair with a separation near 4.3 Å are related by inversion symmetry but there is no symmetry at each R site. The smallest distance between inversion centers is about 9.5 Å.

In spite of the absence of site symmetry, the ground state of each Tm^{3+} ion in TmND appeared to be a non-Kramers doublet with a single g value of 13.59 close to the maximum possible value 13.97, corresponding to the predominantly $|M_J = \pm 6\rangle$ state. The magnetic properties are dominated by the interaction between Tm ions within each dimer, which splits the fourfold ground state of the pair by 0.927 cm⁻¹, corresponding to a nearly pure dipolar interaction (Baker et al. 1986a). An initial splitting of the Tm³⁺ ground state, $\delta_0 \approx 0.17 \text{ cm}^{-1}$, was found by a detailed analysis of EPR spectrum in a single-crystal sphere at temperatures of 1.3 and 0.5 K (Baker et al. 1988). EPR spectra of isolated Tm³⁺ ion in any dilute crystals containing Tm (YND, LaND, PrND and HoND) were not observed at frequencies up to 35 GHz, most probably due to a larger separation δ_0 (Baker et al. 1986b).

An opposite situation takes place for Tb³⁺ ions: the ground state of an isolated Tb³⁺ ion in a dilute LaND (1% Tb) crystal is nearly degenerate, so an EPR spectrum with $g_z = 17.2$, A/h = 6.0 GHz and $\delta_0/h = 8.0$ GHz is observed. EPR in TbND arises only from some type of defect site (Baker et al. 1987).

Measurements of the optical absorption, of magnetic susceptibility between 1.4 and 4.2 K, of EPR between about 9 and 35 GHz in DyND and ErND are consistent with a ground state Kramers doublet close to $|M_J = \pm J\rangle$, an almost Ising-like g tensor, and a purely magnetic dipole-dipole interaction between \mathbb{R}^{3+} ions within a dimeric pair (Baker et al. 1991a,b).

The possibility of magnetic resonance measurements on an impurity in an antiferromagnetic host lattice was discussed by Bleaney (1991). Lanthanide antiferromagnets are convenient materials, since their internal fields for such experiments are of the order of 10 kOe, and the level splittings of paramagnetic ions can be observed in the microwave region, 20–30 GHz. The electron magnetic resonance of impurity Yb^{3+} and Er^{3+} ions was observed in the simple two sublattice antiferromagnet DyPO₄ with Néel temperature $T_N = 3.39$ K (Abraham et al. 1991). Resonance was observed at frequencies of 24 and 34 GHz; the resonance lines were relatively narrow, making it possible to determine the value of the internal field (consisting of dipolar and exchange contributions) acting on each impurity ion. The values of the exchange field are found not to conform to a simple model of an isotropic exchange interaction between the real electron spins of the lanthanide ions.

Antiferromagnetic resonance in single crystals of GdVO₄ (T_N =2.495 K) has been observed by Abraham et al. (1992) at frequencies of 0.035, 17, 24 and 34 GHz. The various magnetic measurements on this model compound show that it is difficult to obtain precise overall agreement with the formulae of the mean field theory.

4.5.2. Transient processes in internal magnetic fields

In this subsection we discuss transient effects, taking into account the fact that quantization axes of different groups of resonant nuclei (with the same or very close resonance frequencies) may be differently oriented (Aminov et al. 1988). We shall again consider the H5A protons in lanthanide ethylsulfates: there are six sets of nuclear spins in internal magnetic fields which are connected with each other through rotations by 60° around the *c*-axis (see fig. 32). The external field H_0 is directed along the *c*-axis (in a ferromagnetic phase it can be lacking), so the values of the effective fields are the same for all six proton sets.

If, as usual, the radiofrequency field H_1 is perpendicular to the constant field H_0 , the amplitudes of fields inducing rotations of magnetic moments will be different for different spin groups. Accordingly, at the end of a rf pulse the moments will be declined to different degrees from their equilibrium directions along the effective fields, and therefore the amplitudes of free induction and echo signals in any case prove to be less than the maximum signal when all spin orientations coincide. An optimum pulse duration at a given geometry of observation can be chosen experimentally.

The situation becomes more complicated when the applied field is not directed along the crystal *c*-axis. Very small deviations lead to the broadening of the single resonance line, which is common for all the spin groups studied, and to accelerated decay of the free induction signal. When deviation increases, the resonance line splits, different spin groups correspond to different components of the spectra, and each component is excited independently. Free induction signals of different spin groups are also independent, but signal amplitudes at a given length of the rf pulse may strongly differ in value, so it is necessary to vary the pulse length for the optimal manifestation of each component.

Under these conditions orientation of the rf field parallel to the field H_0 (i.e., to the *c*-axis) can prove to be preferable. This is certainly so for H5A protons in effective quantizing fields which are almost perpendicular to the *c*-axis, if the applied fields are not too strong (see table 21). In this case the rf field will be equally oriented relative to the quantization axes of all the six proton groups with a given resonance frequency, and

it is not necessary to vary the pulse lengths at small deviations of the applied fields from the crystal axis.

In calculating transient signal amplitudes, it is advisable to introduce three types of coordinate systems:

- (1) The laboratory system with orts e_x , e_y , e_z ; the z-axis is parallel to the crystal c-axis; the x-axis is directed, e.g., along the a-axis.
- (2) A local coordinate system for the *i*-th proton group (e_{ix}, e_{iy}, e_{iz}); the z_i-axis (the quantization axis) is directed along the effective magnetic field on the protons, the x_i-axis is in the xy plane. If θ_i and φ_i are the polar angles of the effective field, that is, e_{iz} = e_{iz}(θ_i, φ_i), then e_{ix} = e_{ix}(π/2, -π/2+φ_i); e_{iy} = e_{iy}(π/2 + θ_i, φ_i) at θ_i < π/2 (see fig. 13); and e_{iy} = e_{iy}(3π/2 θ_i, π + φ_i) at θ_i > π/2.
- (3) A rotating local coordinate system $(e'_{ix}, e'_{iy}, e'_{iz})$,

$$e'_{iz} = e_{iz}, \qquad e'_{ix} = e_{ix}\cos(\omega t + \alpha_i) + e_{iy}\sin(\omega t + \alpha_i), e'_{iy} = -e_{ix}\sin(\omega t + \alpha_i) + e_{iy}\cos(\omega t + \alpha_i).$$
(262)

Here ω is the frequency of the alternating field, which is close to the resonance frequency ω_0 , and it is advisable to choose a phase α_i in such a way that $e'_{ix}(t=0)$ would be directed along the projection H^0_{1i} of the rf field $H_1(t) = H^0_1 \cos \omega t$ on the (x_i, y_i) -plane.

An rf pulse which is switched on at t=0, declines the magnetic moment $M_{i0}(0) = M_0 e_{iz}$ of the *i*-th spin group from its equilibrium direction. At resonance conditions the moment rotates around the axis e'_{ix} , so at the end (t_1) of the pulse

$$M'_{ix} = M_i e'_{ix} = 0, \qquad M'_{iy} = -M_0 \sin \omega_i t_1, \qquad M'_{iz} = M_0 \cos \omega_i t_1,$$

where $\omega_i = \gamma H_{1i}^0/2$, $H_{1i}^0 = H_1^0 e'_{ix}(t=0)$. As a result, a moment oscillating with the resonance frequency arises in the laboratory system at $t > t_1$,

$$M(t) = \sum_{i} M_{i}(t) = \sum_{i} (M_{i}e'_{i\gamma})(e'_{i\gamma}e_{i\beta})(e_{i\beta}e_{\alpha})e_{\alpha}$$

= $M_{0}\sum_{i} \cos \omega_{i}t_{1}(e_{iz}e_{\alpha})e_{\alpha}$
+ $M_{0}\sum_{i} \sin \omega_{i}t_{1} \left[\sin(\omega_{0}t + \alpha_{i})(e_{ix}e_{\alpha}) - \cos(\omega_{0}t + \alpha_{i})(e_{iy}e_{\alpha})\right]e_{\alpha}.$ (263)

Here the first sum is a constant part of the moment, the sum over i includes spin groups with equal resonance frequencies.

In the initial model with six proton groups all the θ 's coincide with each other, $\theta_i = \theta$, $\phi_i = \frac{1}{3}\pi(i-1)$ (fig. 31). To illustrate the arguments given at the beginning of the present subsection, we shall consider alternating fields directed along the x- and z-axes.

(a) $H_1^0 = H_1^0 \boldsymbol{e}_x$. In this case $H_{1i}^0 = H_1^0 (\sin \phi_i \boldsymbol{e}_{ix} + \cos \theta \cos \gamma_i \boldsymbol{e}_{iy})$, therefore

$$\omega_1 = \omega_4 = \frac{1}{2} \gamma H_1^0 \cos \theta = \omega' \cos \theta, \qquad \omega_{2,3,5,6} = \frac{1}{2} \omega' (3 + \cos^2 \theta)^{1/2}.$$

Furthermore, it follows from eq. (262) that

$$\cos \alpha_i = \left(\frac{H_1^0}{H_{1i}^0}\right) \sin \phi_i, \qquad \sin \alpha_i = \left(\frac{H_1^0}{H_{1i}^0}\right) \cos \theta \cos \phi_i.$$

The components of the oscillating moments according to eq. (263) are equal to

$$\frac{M_x(t)}{M_0} = \frac{\sin \omega_0 t}{\omega} \sum_i \omega_i \sin \omega_i t_1,$$

$$\frac{M_y(t)}{M_0} = -\omega' \sin^2 \theta \sin \omega_0 t \sum_i \frac{\sin \omega_i t_1}{\omega_i} \sin \phi_i \cos \phi_i$$

$$-\omega' \cos \theta \cos \omega_0 t \sum_i \frac{\sin \omega_i t_1}{\omega_i},$$

$$\frac{M_z(t)}{M_0} = -\omega' \sin \theta \cos \theta \sin \omega_0 t \sum_i \frac{\sin \omega_i t_1}{\omega_i} \cos \phi_i$$

$$+\omega' \sin \theta \cos \omega_0 t \sum_i \frac{\sin \omega_i t_1}{\omega_i} \sin \phi_i.$$
(264)

If $\theta = 0$ (all spins are quantized along the z-axis) all $\omega_i = \omega'$, as prescribed, and

$$M_x(t) = 6M_0 \sin \omega' t_1 \sin \omega_0 t, \qquad M_y(t) = -6M_0 \sin \omega' t_1 \cos \omega_0 t,$$

i.e., one has a rotating magnetic moment which attains a maximum amplitude of $6M_0$ at pulse length $\omega' t_1 = \pi/2$.

On the contrary, if θ is close to $\pi/2$, as in the case of the H5A protons in TbES, the values of ω_1 and ω_2 are considerably different, that is, different pulse lengths are needed for excitation of spin groups 1, 4 and 2, 3, 5, 6.

(b)
$$H_1^0 = H_1^0 e_z$$
. Now $H_{1i}^0 = -H_1^0 \sin \theta e_{iy}$, $\omega_{1-6} = \omega' \sin \theta$, $\alpha_1 = -\pi/2$; hence

$$\frac{M_x(t)}{M_0} = -\cos \omega_0 t \sin \omega_1 t_1 \sum_i \sin \phi_i - \sin \omega_0 t \sin \omega_1 t_1 \cos \theta \sum_i \cos \phi_i,$$

$$\frac{M_y(t)}{M_0} = \cos \omega_0 t \sin \omega_1 t_1 \sum_i \cos \phi_i - \sin \omega_0 t \sin \omega_1 t_1 \cos \theta \sum_i \sin \phi_i,$$

$$\frac{M_z(t)}{M_0} = \sin \omega_0 t \sin \omega_1 t_1 \sin \theta s,$$

(265)

where $s = \sum_{i} 1$ is the number of resonating protons per one lanthanide ion. As can be seen, for maximum excitation of each spin group the pulse length must be the same,

 $\omega_1 t_1 = \pi/2$. If all the spins resonate and the sum over *i* includes all the six spin groups, the sums with $\sin \phi_i$ and $\cos \phi_i$ vanish in eqs. (264) and (265). The signal in case (a) proves to be elliptically polarized, and in case (b) linearly polarized.

4.5.3. Magnetic resonance line shape

As mentioned above, the molecular fields in ferromagnetic crystals are extremely inhomogeneous, and therefore the nuclei in different crystallographic positions are affected by fields with different magnitudes and directions. So the nuclei have different resonance frequencies, which form a broad NMR spectrum. In the present subsection we shall consider the separate line width of the proton resonance spectrum in ethylsulfates.

The very fact of observing the proton spin echo in the absence of an external field or in a homogeneous applied field bears evidence to inhomogeneous broadening of an individual line of proton magnetic resonance. It was shown experimentally (Aminov et al. 1988) that the spin echo shape has a Gaussian form

$$A(t) = A(2\tau) \exp\left[-\left(\frac{t-2\tau}{T_2^*}\right)^2\right]$$
(266)

with characteristic T_2^* times of the order of 4-8 µs. The decay of spin echo at ultralow temperatures (down to 70 mK) can also be approximated by the Gaussian curve,

$$A(2\tau) = A(0) \exp\left[-\left(\frac{2\tau}{T_2}\right)^2\right].$$
(267)

A Fourier image of the curve (266) gives an idea about the inhomogeneously broadened line shape. The solid curves in fig. 34 show the H5A NMR line shapes in TbES and DyES samples in zero external field. It is natural to assume that inhomogeneous broadening is a consequence of crystal structure distortions. There are at least three broadening mechanisms. One of them is due to the random variations of the proton coordinates in the inhomogeneous internal magnetic field of a crystal. In a real crystal lattice distorted by defects, a certain dispersion of molecular fields corresponds to slightly scattered nuclear positions. Assuming that the value of the dispersion $\delta H \approx \delta r |dH_{loc}/dr|$ is equal to the observed NMR linewidth, and taking into account the pure dipolar nature of local fields $(H_{loc} \approx \mu_B r^{-3})$, one obtains an uncertainty of the H5A proton coordinates

$$\frac{\delta r}{r} \approx \frac{\delta H}{3H_{\rm loc}} \approx 3 \times 10^{-3}.$$
(268)

This value is close to the error in determining the proton coordinates in the YES lattice by Broach et al. (1979).

The second mechanism of broadening is also due to the random displacements of atoms in the lattice, but it is manifested by means of variations of lanthanide magnetic moments from one lattice site to another, because of the random distortion of the crystalline



Fig. 34. Shape of H5A NMR lines in ferromagnetic crystals; (a) TbES: T = 0.16 K; $H_0 = 0$; $T_2^* = 4.1 \,\mu$ s; $T_2 = 60 \,\mu$ s. (b) TbES: T = 0.16 K; $H_{0z} = 1600$ Oe; $T_2^* = 2.7 \,\mu$ s. A and B are the two components of a spectrum split due to the small deviation of the applied field from the crystal *c*axis; A, frequency 16.58 MHz; $T_2 = 96 \,\mu$ s; B, frequency 15.9 MHz; $T_2 = 220 \,\mu$ s. (c) DyES: T = 0.075 K, $H_0 = 0$; $T_2^* = 6 \,\mu$ s; $T_2 = 80 \,\mu$ s. Solid curves, inhomogeneously broadened NMR lines; dashed curves, homogeneously broadened NMR lines.

potential. In the case of a TbES crystal a weak distortion of the crystalline potential affects primarily the value δ_0 of an initial splitting of quasidoublet states, but it exerts almost no influence on the g_{\parallel} value, while only the scatter of the *g*-value of the Dy³⁺ ion ground doublet can be a cause of inhomogeneous NMR broadening in a DyES crystal according to this mechanism. The inhomogeneous NMR linewidths of H5A nuclei in both crystals are very close in relative units, $\delta\omega/\omega_0 = 9 \times 10^{-3}$.

The sixth-order terms B_{60} , $B_{66} \propto \Sigma r_j^{-7}$ are to be the most sensitive to variations of ligand coordinates. Assuming $\delta r/r \approx 3 \times 10^{-3}$ (cf. eq. 268) to be the uncertainty in the coordinates of O^{2-} ions, we obtain a scatter of the B_{60} and B_{66} parameters of the order of 2–3%. A direct calculation of the crystalline Stark effect shows that just such a scatter of the C_{66} parameters is sufficient for an explanation of both the spread $|\Delta\delta|$ of the lowest energy levels of Tb³⁺ ion and the spread Δg of the Dy³⁺ ion g-factor. These spreads determine the observed inhomogeneous broadening of the proton magnetic resonance lines.

The third mechanism of inhomogeneous NMR line broadening in lanthanide ethylsulfates is due to the presence of nuclear spins with different resonance frequencies. For instance, the H5B proton plays the role of an "alien spin" relative to the H5A proton in the same H_2O molecule. The nuclear moments of lanthanide ions are also classified as alien spins. In DyES crystals their influence on inhomogeneous broadening of the proton magnetic resonance lines is not revealed, due to the small natural abundance of odd ^{161,163}Dy isotopes and to relatively weak hyperfine interaction. On the contrary, in the TbES crystal the contribution of ¹⁵⁹Tb nuclear moments (natural abundance 100%, spin $I = \frac{3}{2}$) into inhomogeneous proton resonance linewidth appears to be significant. Due to the hyperfine interaction AS_zI_z , the lowest energy level of the Tb³⁺ quasidoublet splits into four equidistant nuclear sublevels, separated by intervals A/2. At temperatures comparable with $A/k_{\rm B} = 0.3$ K ¹⁵⁹Tb nuclear moments are disordered, and the effective internal fields on the H5A protons from near the different Tb³⁺ ions are slightly different. When temperature is decreased, terbium nuclear spins are polarized, and this source is no longer active; in fact the proton resonance line broadening due to terbium nuclei must become negligible at $T \leq 0.07$ K.

A Fourier transform of curve (267) corresponds to homogeneously broadened NMR lines; examples are shown by dashed lines in fig. 34. An external magnetic field does not change the NMR line shape, but strongly affects linewidths: it follows from figs. 34a,b that when the field is switched on, the inhomogeneous linewidth is increased and, on the contrary, the homogeneous width is decreased. The two dashed curves in fig. 34b reflect the line splitting due to the small deviation of an applied field H_0 from the strict parallel orientation (cf. eq. 257).

A detailed picture of the irreversible decay of transverse magnetization seems to be highly complicated in view of the different roles of different nuclei groups in the decay. Thus, when the H5A proton relaxation in ethylsulfate is studied, the fact that the strongest field (about 4 Gauss) on the H5A proton is created by its neighbour in a water molecule, that is, the H5B proton, should be taken into account; the rate of these field fluctuations (an inverse lifetime of the H5B proton in a "stationary" state, which is determined by the interaction with other H5B protons) is of the order of 10^4 s^{-1} . H4 protons give rise to smaller fields (about 1 Gauss), which, however, have a greater fluctuation rate, $\sim 10^5 \text{ s}^{-1}$, because similar protons are placed at very small distances (within one water molecule), etc.

When the lineshape is known, the T_2 time can be estimated by calculating the second moment of a resonance line; however the ordinary procedure of the calculation (Al'tshuler and Kozyrev 1972) must be modified in such a manner as to take into account the scatter of quantization axis orientations for different nuclear spins. Let us write down the Zeeman Hamiltonian of nuclei with the resonance frequency ω_0 in the form

$$\mathcal{H}_{\mathbf{Z}} = -\omega_0 \sum_{P_i} I_{P_{iz}},\tag{269}$$

where P is the lanthanide ion number; *i* labels nuclei with a given resonance frequency surrounding the lanthanide ion (for example, H5A protons with i=1-6 at $H_0||c$ as shown in fig. 31; we shall keep this model in mind), I_{Piz} is the projection of the nuclear spin Pi on the z_i -axis of the local coordinate system directed along the effective field H_i on the spin

(fig. 17). The secular part of the magnetic dipole–dipole interaction Hamiltonian relative to \mathcal{H}_Z has the following form:

$$\mathcal{H}_{sec} = \frac{\gamma^{2} \hbar^{2}}{2} \sum_{PiQj} \frac{1}{r^{3}} \left[B_{PiQj} I_{Piz} I_{Qjz} + (C_{PiQj} I_{Pi+} I_{Qj-} + \text{H.c.}) \right] + \gamma^{2} \hbar^{2} \sum_{PiQj} \frac{1}{r^{3}} B_{PiQj'} I_{Piz} I_{Qj'z},$$
(270)

where the first sum is over all the pairs of nuclear spins with the resonance frequency ω_0 , index Qj' in the second sum refers to nuclei with other resonance frequencies;

$$B_{PiQj} = (e_{iz}e_{jz}) - 3r^{-2}(e_{iz}r)(e_{jz}r), \qquad C_{PiQj} = (E_{i+}E_{j-}) - 3r^{-2}(E_{i+}r)(E_{j-}r),$$

$$E_{i\pm} = \frac{1}{2}(e_{ix\pm}e_{iy})$$

Depending on the orientation of the alternating field (α), the second moment of a resonance line is:

$$\hbar^2 M_2^{(\alpha)} = -\frac{\operatorname{Sp}\left[\mathcal{H}_{\operatorname{sec}}, \tilde{I}_{\alpha}\right]^2}{\operatorname{Sp}\tilde{I}_{\alpha}^2},\tag{271}$$

where \tilde{I}_{α} is the "truncated" part of the projection on α of the total moment of the resonance nuclei:

$$\tilde{I}_{\alpha} = \sum_{Pi} \left(\beta_{i\alpha} I_{Pi+} + \text{H.c.} \right), \qquad \beta_{i\alpha} = (\boldsymbol{E}_{i+} \boldsymbol{e}_{\alpha}), \tag{272}$$

i.e. the truncation is achieved by projecting the α -components of the operators I_{Pi} on planes which are perpendicular to the z_i -axes of the local coordinate systems; e_{α} is an ort of direction α . After calculating commutators and traces, the second moment is reduced to lattice sums

$$M_{2}^{(\alpha)} = \frac{\gamma^{4}\hbar^{2}}{3}I(I+1)\left(\sum_{Qj} \frac{1}{r^{6}} \left|R_{PiQj}^{\alpha}\right|^{2} + \sum_{Qj'} \frac{1}{r^{6}} \left|R_{PiQj'}^{\prime\alpha}\right|^{2}\right) \left(\frac{1}{s}\sum_{i} \left|\beta_{i\alpha}\right|^{2}\right)^{-1}, \quad (273)$$

where $R_{PiQj}^{\alpha} = B_{PiQj}\beta_{i\alpha} - 2C_{PiQj}\beta_{j\alpha}$, $R_{PiQj'}^{\prime \alpha} = B_{PiQj'}\beta_{i\alpha}$; s is the number of resonant spins per lanthanide ion; the indices *i*, *j*, as earlier, refer to resonant nuclei, and *j'* to nonresonant ones. If the quantization axes of all nuclear spins coincide, eq. (273) is reduced to the usual formula for M_2 .

If the rf field H_1 is directed along the x-axis, $\beta_{ix} = (-\sin \phi_i + i \cos \theta_i \cos \phi_i)$, and if $H_1 || z(c)$, then $\beta_{iz} = -\frac{1}{2}i \sin \theta_i$, where θ_i , ϕ_i are polar angles of the z_i -axis of the local coordinate system. In the latter case the geometric factor β , which is the same for all

resonant nuclei (keeping in mind that the applied field H_0 is directed along the *c*-axis or close to it), is cancelled in the numerator and denominator of eq. (273), thus one has

$$M_{2}^{(\alpha)} = \gamma^{4} \hbar^{2} (S + U + V), \qquad S = \sum_{Qj} \frac{1}{r^{6}} |B_{PiQj}|^{2} + \sum_{Qj'} \frac{1}{r^{6}} |B_{PiQj'}|^{2},$$

$$U = 4 \sum_{Qj} \frac{1}{r^{6}} |C_{PiQj}|^{2}, \qquad V = -2 \sum_{Qj} \frac{1}{r^{6}} B_{PiQj} (C_{PiQj} + C_{PiQj}^{*}).$$
(274)

For the H5A protons, as mentioned above, the index j at each value of Q (the lanthanide ion number in a crystal) runs over six values if the applied field H_0 is directed exactly along the z-axis and all the H5A protons have the same resonance frequency. When H_0 deviates from the z-axis, the index j takes one or two values, depending on the azimuthal direction of the field.

Calculations according to eq. (274) for H5A protons in ferromagnetic TbES in the absence of an applied magnetic field, result in a value of $M_2/\gamma^4\hbar^2$ equal to $\sim 0.20 \times 10^{46}$ cm⁻⁶ which at Gaussian lineshape corresponds to the lifetime

$$T_2 = \left(\frac{2}{M_2}\right)^{1/2} \approx 0.42 \times 10^{-4} \,\mathrm{s.}$$
 (275)

To simplify the calculations we have restricted ourselves to the interaction of similar protons only, in other words, the second part (the sum over Qj') in S-sums (274) has been discarded. In view of the crudeness of the above approximation, the agreement of eq. (275) with the corresponding experimental value $T_{2\exp} = 0.7 \times 10^{-4}$ s can be regarded as satisfactory. The coincidence in the order of magnitude of the calculated values T_2 with experimental data is convincing evidence that the decay of the spin echo signal at extremely low temperatures is indeed due to the magnetic dipole–dipole interaction between protons.

4.6. Magnetic relaxation in ordered and non-ordered phases

The inhomogeneous NMR linewidth in ferromagnets does not change much with an increase of temperature, as experiments on proton spin echo in TbES and DyES have shown (Aminov et al. 1988). At the same time a homogeneously broadened line remains invariable at low temperatures, but broadens strongly with increasing temperature, taking the Lorentzian shape. These changes start to appear at temperatures $T \approx \frac{1}{10} \delta$, where δ is the splitting of the lanthanide ion energy levels (in degrees Kelvin) in the effective field $H_z^R = H_M^R + H_{0z}$. The temperature-dependent part of the relaxation rate T_2^{-1} for H1 and H5A protons can be presented as

$$T_2^{-1} = S \exp\left(\frac{-\delta}{T}\right). \tag{276}$$

At temperatures $T \ge 0.2\delta$ the fluctuations of internal magnetic fields enhance the relaxation of the transverse nuclear magnetization to such an extent, that the observation

of spin echo becomes impossible. The homogeneous broadening of the proton magnetic resonance lines due to the fluctuations of internal magnetic fields in TbES and DyES crystals occurs almost identically: the pre-exponential factors S for both crystals are within the limits of 10^7-10^8 s^{-1} . No explicit magnetic field dependence of the S value in TbES has been revealed in measurements at different frequencies.

The investigation of the longitudinal magnetization relaxation for the H1 and H5A protons in both crystals TbES and DyES has shown that one has to approximate the recovery of the magnetization after the rf pulses by the two-exponential law,

$$1 - \frac{A_t}{A_{\infty}} = \lambda \exp\left(-\frac{t}{T_1'}\right) + (1 - \lambda) \exp\left(-\frac{t}{T_1''}\right), \qquad (277)$$

where the parameter λ is close to unity. The fast relaxation with a characteristic time T'_1 has been interpreted as an establishment of thermal equilibrium between the nuclei under consideration and the dipole-dipole reservoir of lanthanide ions, while other possible processes of the energy exchange in the crystal have been referred to as the "slow relaxation", proceeding within a time T''_1 . For example, these processes involve the establishment of equilibrium between the dipole-dipole reservoir and the electronic Zeeman reservoir and crystal lattice, an energy exchange between different nuclei groups due to the nuclear spin diffusion in the fluctuating magnetic fields (Horvitz 1971, Wolfe 1973). In such a case just the time of the fast relaxation gives a possibility of estimation of electron spin-spin relaxation rate for lanthanide ions.

The temperature dependence of the fast relaxation rate of protons in the whole range of the observation temperatures, is described by the exponential law

$$T_1^{-1} = S_1 \exp\left(-\frac{\delta}{T}\right),\tag{278}$$

the exponent index being in satisfactory agreement with the splitting of the low-lying energy levels of Tb^{3+} or Dy^{3+} ions. As has been expected, no anomalies of T_1 are observed in the temperature region near T_C at high external magnetic fields, since in this case a high degree of electronic polarization is achieved already in the paramagnetic phase.

The resonance of the H5A protons in ferromagnetic crystals can be observed even without an external field. In the TbES crystal at temperatures 0.20 K < T < 0.22 K, which are adjacent from below to the phase transition point, an anomalous behaviour of the relaxation is observed: its rate falls somewhat when the temperature approaches $T_{\rm C} = 0.24 \text{ K}$. Too short times T_2 prevent the measurements of the H5A proton relaxation in the DyES crystal in the immediate proximity to $T_{\rm C} = 0.118 \text{ K}$.

The field dependence $T_1^{-1}(H)$ has also been investigated for H5A nuclei in paramagnetic crystals TbES (at T = 0.29 K) and DyES (T = 0.135 K) and in ferromagnetic TbES (T = 0.16 K). The measurement results are given in figs. 35 and 36. The data for DyES are well approximated by the expression

$$T_1^{-1} = 2.6 \times 10^6 \exp\left[-\frac{10.8\mu_{\rm B}(H_{0z} + 375{\rm Oe})}{0.135k_{\rm B}}\right]$$
(279)

(the straight line in fig. 35).



Fig. 35. Relaxation rate of the longitudinal magnetization of H5A protons in TbES (open circles, T = 0.29 K), and DyES (open triangles, T = 0.135 K) paramagnetic crystals, as a function of the external field H_{0z} ; the straight line is described by eq. (279) (Aminov et al. 1988).

Fig. 36. Relaxation rate of H5A-proton longitudinal magnetization in ferromagnetic TbES as a function of the external field H_{0z} (Aminov et al. 1988); temperature, 0.16 K; resonance frequency, 15.2–15.9 MHz.

We note that the constant relaxation rate in a ferromagnetic sample of TbES at external fields from 0 to 500 Oe (fig. 36) indicates that the internal magnetic field in the crystal

is conserved. Apparently, an external field inclined to the *c*-axis still penetrates into the crystal, but slightly affects the internal field. Contrary to T_1 , the T_2 time proves to be sensitive to these small changes, due to the fact that an inclined field (even a weak one) lifts the degeneracy of the NMR line. The difference between the T_1 and T_2 sensitivities to the inclined fields is retained at high fields H_0 too. For instance, the T_2 times, measured at T=0.17 K and at a single value of field $H_0=1600$ Oe for different components of the H5A spectrum, differ markedly: for frequencies 16150, 16450, 16600, and 16950 kHz they are equal to 245, 160, 116, and 260 µs, respectively, whereas the longitudinal relaxation measurements at T=0.17 K for all four components give approximately the same time $T_1 \approx 2.5-3$ s.

Apparently, the proton relaxation mechanism at temperatures, for which eqs. (276) and (278) hold, is connected with thermal excitations of the matrix ions Tb³⁺ and Dy³⁺. However, as distinct from VV paramagnets it is unclear beforehand, whether the conditions of both the strong narrowing and fast fluctuations will be fulfilled in this case. Aminov et al. (1988, 1990c) have suggested a simple generalization of the formulae for the relaxation times of nuclear spins, which is prompted by the comparison of eq. (174) for T_2^{-1} in the case of fast fluctuations and eq. (169) for the line width Γ in the adiabatic theory at arbitrary fluctuation rates. Namely, we substitute $j_{\beta\beta'}(\Delta\omega_i)$ for $j_{\beta\beta'}(0)$ and, by analogy, $j_{\beta\beta'}(\omega_0 + \Delta\omega_i)$ for $j_{\beta\beta'}(\omega_0)$ in eq. (174), where $\Delta\omega_i = [(\omega_0 + \Delta\omega_{il})^2 + \Delta\omega_{il}^2]^{1/2} - \omega_0$ is an NMR frequency shift due to the change of an orientation of the *i*-th lanthanide ion magnetic moment; $\Delta\omega_{il} = 2\gamma h_{il}$, $\Delta\omega_{il} = 2\gamma h_{il}$, h_{il} and h_{it} are the local field components, parallel and perpendicular to the quantization axis of the nuclear spin. In the general case the orientation of an effective quantizing field is defined by the polar angles θ_M and ϕ_M , and the contributions of the *i*-th ion to the local field can be presented in the form of

$$h_{il} = \left(\frac{g_{\parallel}\mu_{\rm B}}{2r^3}\right) \left[(1 - 3\cos^2\theta_i)\cos\theta_{\rm M} - 3\sin\theta_i\cos\theta_i\cos(\phi_i - \phi_{\rm M})\sin\theta_{\rm M} \right], \quad (280)$$
$$h_{it} = \left(\frac{g_{\parallel}\mu_{\rm B}}{2r^3}\right) \left\{ 9\cos^2\theta_i\sin^2\theta_i\sin^2(\phi_i - \phi_{\rm M}) + \left[(1 - 3\cos^2\theta_i)\sin\theta_{\rm M} + 3\sin\theta_i\cos\theta_i\cos(\phi_i - \phi_{\rm M})\cos\theta_{\rm M} \right]^2 \right\}^{1/2}$$
(281)

Here we use the coordinate system, in which the axes x and z are directed along the crystallographic a and c axes, respectively; the nucleus under study is placed at the origin; r_i , θ_i , ϕ_i , are the polar coordinates of the *i*-th lanthanide ion. Now the nuclear relaxation rates can be written in the appropriate form

$$T_1^{-1} = \sum_i \frac{\Delta \omega_{it}^2 \tau}{1 + (\omega_0 + \Delta \omega_i)^2 \tau^2} \exp\left(-\frac{\Delta}{k_{\rm B}T}\right),\tag{282}$$

$$T_2^{-1} = \sum_i \left[\frac{1}{2} \frac{\Delta \omega_{it}^2 \tau}{1 + (\omega_0 + \Delta \omega_i)^2 \tau^2} + \frac{\Delta \omega_{il}^2 \tau}{1 + \Delta \omega_i^2 \tau^2} \right] \exp\left(-\frac{\Delta}{k_{\rm B}T}\right),\tag{283}$$

where τ is the electron relaxation time of the lanthanide ion. If the fluctuations of the molecular field at the nucleus are caused mainly by one lanthanide ion (the nearest one with the number 1), so that $\Delta \omega_{1l} \gg \Delta \omega_{il}$ ($i \neq 1$), $\Delta \omega_{1l} \tau \gg 1$, $\Delta \omega_{il} \tau \ll 1$, then eq. (283) is reduced approximately to

$$T_2^{-1} \approx \tau^{-1} \exp\left(-\frac{\delta}{k_{\rm B}T}\right)$$

The roughest assumption, used for writing down the above formulae, is concerned with the independence of fluctuations of local fields due to separate lanthanide ions. However, in quasi-one-dimensional ferromagnets TbES and DyES the excitations in neighbouring axial chains are weakly coupled to each other, so one can count, at least, upon the qualitative interpretation of the experiments.

An analysis of the experimental data by means of eqs. (280)–(283) makes it possible to conclude that the fluctuation rate τ^{-1} for the Tb³⁺ ion states actually does not depend on the value of an applied field and equals approximately $2 \times 10^7 \text{ s}^{-1}$. For the Dy³⁺ ions in DyES $\tau^{-1} \approx 0.25 \times 10^7 \text{ s}^{-1}$.

In magnetically diluted crystals the role of τ is usually played by the electron spinlattice relaxation time τ_1 . King et al. (1972) dealt precisely with such a situation; they measured the rate of longitudinal relaxation of the H5B protons in a YES:Yb³⁺ crystal in the temperature range of 1.4–2.4 K and then, knowing the exact temperature dependence of the Yb³⁺ spin-lattice relaxation rate ($\tau^{-1}=0.0135T^9$) and the value h_t of fluctuating magnetic field transverse component, directly confirmed the well-known formula for the rate of the nuclear spin relaxation via paramagnetic impurity,

$$T_1^{-1} = \left(\frac{h_t}{H_0}\right)^2 \tau_1^{-1} (1 - P_0^2), \tag{284}$$

where P_0 is the polarization of an ion. In this case eq. (282) comprises a single term, which is also reduced to the formula (284).

The values τ , found for TbES and DyES crystals, are much shorter than the electron spin-lattice relaxation times at the observed temperatures; in these magnetically concentrated crystals they are certainly defined by spin-spin relaxation processes. However, an estimation of the Tb³⁺ ion excited state lifetime by means of eq. (171), using the magnetic dipole-dipole interaction, results in the value $\tau^{-1} = 2.45 \times 10^9 H_z^{-4} \text{ s}^{-1}$ (H_z in units of kOe) (strongly depending on the magnetic field), that is, in the range of fields $H_{0z} = 295-855$ kOe, used in experiments, the correlation time should change by two orders of magnitude. Possibly, the observed smoothing of the field dependence is explained by the fact that the energy transfer between ions is realized by means of interactions via the phonon field, which is comparable to the dipole-dipole interactions in ethylsulfates (see Baker 1971, Krygin and Prokhorov 1984).

In the case of DyES the matrix elements of $\mathcal{H}_{dip-dip}$ on the ground doublet functions are zero. Therefore the spin-spin relaxation rate will differ from zero, due only to the

mixing of wave functions of the ground doublet and excited doublet with the energy $\Delta = 16.3 \text{ cm}^{-1}$. In its turn, such mixing may be due to small distortions of the crystal potential because of different structural defects. As a result the g_{\perp} -factor differs from zero. This effect was mentioned by Wolfe and Jeffries (1971) for Yb³⁺ ions in YES, which suggested an estimate of $g_{\perp} \approx 0.01$. To achieve an agreement with the experimental value of the correlation time for the Dy³⁺ ion in DyES, it is necessary to assume the larger value of the transverse component of the ion, $\langle g_{\perp}^2 \rangle^{1/2} \approx 0.10$. The contribution of the interaction via the phonon field to the energy migration rate for the Kramers ion Dy³⁺ must be less than that for Tb³⁺ ion.

5. Mixed crystals

In the Introduction it has already been mentioned that different lanthanide compounds usually constitute homologous series with similar crystal lattice structure, and they can be synthesized by varying the lanthanide ion concentration in the entire range from 0 to 100%. Studies of disordered media, particularly of their phase transitions, represent one of the most interesting trends of modern solid state physics. Detailed investigations of phase diagrams, of static and dynamic critical properties of solid solutions of lanthanide compounds have been carried out since the seventies. The mixed and diluted crystals with zircon (RMO_4) and scheelite structure (double fluorides $LiRF_4$), have mainly been studied as model systems for the verification of modern theoretical concepts on critical phenomena in disordered solids. We shall further identify as "mixed" the systems containing two different lanthanides or any other two different chemical elements, if both pure compounds have undergone phase transitions. If the phase transition is induced by only one kind of lanthanide ion of the rare-earth sublattice, the system will be referred to as "dilute".

Since the relative differences of ionic radii of trivalent lanthanide ions are small (within 8% for the second half of the lanthanide group from Gd to Lu), it is possible to disregard correlations between the occupation numbers $c_{\rm R}(\lambda M)$ of the lattice points, introduced in the sect. 2.1, and to consider them as independent random variables. On the other hand, the differences between the ionic radii of the matrix and impurity ions are responsible for the local deformations of a crystal lattice; the structural disorder of a crystal results in a random crystal field. As has been demonstrated in the sect. 3.5, the influence of impurity rare-earth ions on spectral characteristics of neighbouring lanthanide ions may be significant. Therefore interionic interactions in mixed and diluted crystals have a random character, not only because of the explicit dependence on the occupation numbers $c_{\rm R}(\lambda M)$, but also because of the random spatial variations of the energy spectra (Stark splittings, g-factors) of separate ions. We must note such effects of the random fields as smearing of anisotropy constants, alteration of static and dynamic critical behaviour (qualitatively determined by the reduction of an effective dimensionality of a system) domain freezing, and emergence of new phases both in the absence and in the presence of an applied magnetic field.

A new interesting problem, inherent to the physics of disordered materials, is the investigation of a mixed system near the critical concentration dividing the regions of existence of different phases. It should also be noted that the percolation approach is inappropriate for describing the mixed and diluted crystals of lanthanide compounds, since their properties are determined mainly by long-range magnetic dipole–dipole interactions and interactions through the acoustic phonons. On the contrary, there are reasons to use the self-consistent field approximation.

First we give a brief summary of experimental investigations, carried out heretofore. Two sets of crystals, {TmVO₄, TbVO₄, TmAsO₄, TbAsO₄} and {DyVO₄, DyAsO₄}, are proper ferroelastics with the order parameters $e(B_{2g})$ and $e(B_{1g})$, respectively (see tables 8 and 22). Structural phase transitions $D_{4h}^{19} \rightarrow D_{2h}^{28}$, $D_{4h}^{19} \rightarrow D_{2h}^{24}$ are induced by the cooperative Jahn–Teller effect and accompanied by the ordering of Tm³⁺, Tb³⁺, Dy³⁺ electron multipoles of corresponding symmetry. The DyPO₄ and GdVO₄ crystals are the two-sublattice Ising antiferromagnets with the magnetic moments $\boldsymbol{\mu} \parallel c$; DyVO₄ and DyAsO₄ are the four-sublattice Ising antiferromagnets, $\boldsymbol{\mu} \parallel b$; LiHoF₄ and LiTbF₄ are the Ising ferromagnets.

as functions of the concentration p of the lanthanide ions, active in stimulating the longrange order, were measured in the following systems: System Reference(s)

The transition temperatures of structural $(T_D(p))$ and magnetic $(T_N(p), T_C(p))$ ordering,

Dilute	evetome

$T_{\rm D}(p)$	$Tm_pLu_{1-p}VO_4$	Gehring et al. 1976b
	$\mathrm{Tb}_p\mathrm{Yb}_{1-p}\mathrm{VO}_4$	Pilawa et al. 1988
	$\mathrm{Tb}_p\mathrm{Gd}_{1-p}\mathrm{VO}_4$	Glynn et al. 1977, Harley et al. 1974
	$Dy_pY_{1-p}VO_4$	Harley et al. 1974
	$Dy_pGd_{1-p}VO_4$	Bingham et al. 1984b
$T_{\rm C}(p)$	$LiHo_pY_{1-p}F_4$	Reich et al. 1986, 1987, 1990, Jensen and Kjaer 1989, Rosenbaum et al. 1991, Wu et al. 1993
	$LiTb_pY_{1-p}F_4$	Folkins et al. 1982, Mennenga et al. 1985, Kjaer et al. 1989
	$(\mathrm{Tm}_p\mathrm{Y}_{1-p})_2(\mathrm{SO}_4)_3\cdot 8\mathrm{H}_2\mathrm{O}$	Simizu and Friedberg 1982, 1983

Mixed systems with similar types of structural or magnetic ordering

$T_{\rm D}(p)$	$Tb_pTm_{1-p}VO_4$	Pilawa et al. 1988		
	$Tb_pTm_{1-p}AsO_4$	Kasten et al. 1987		
$T_{\rm C}(p)$	$LiHo_n Tb_{1-n}F_4$	Griffin et al. 1981		

NONMETALLIC LANTHANIDE COMPOUNDS

$T_{\rm D}(p)$	$\mathrm{Tb}_p\mathrm{Dy}_{1-p}\mathrm{VO}_4$	Vasil'ev et al. 1989, Hess et al. 1990, Sokolov et al. 1992b
$T_{\rm N}(p)$	$Dy_pGd_{1-p}VO_4$	Bingham et al. 1984b

Mixed systems with competitive order parameters

The influence of random crystal fields on the transition temperature and critical behaviour has also been studied for systems with structural disorder in their matrix, although with a regular lanthanide sublattice:

	System	Reference(s)
$T_{\rm D}(p)$	$Dy(V_pAs_{1-p})O_4$	Graham et al. 1987, 1991a,b, Taylor et al. 1986, Reza and Taylor 1992
$T_{\rm N}(p)$	$Dy(V_pP_{1-p})O_4$	Dirkmaat et al. 1987

Long-range order in systems with different types of order parameters is often suppressed at small concentrations of the impurity ions. Reduction of the transition temperature and breakdown of the ordered state may be caused by the strong coupling of the order parameter with the field of random lattice deformations. In an early investigation of diluted compounds with the cooperative Jahn-Teller effect, Gehring et al. (1976b) described the very rapid reduction in the transition temperature of the $Tm_pLu_{1-p}VO_4$ crystal with the increase of concentration of the impurity Lu ions within the framework of the molecular field theory. The free energy of the diluted lanthanide subsystem was averaged with the Gaussian distribution function for random splittings of the ground non-Kramers doublet of the Tm³⁺ ion. The width of the Gaussian distribution was chosen so as to fit the calculation results to the measurement data. Only the random deformation of the same symmetry as the order parameter has been taken into account. The results of the measurements by Pilawa et al. (1988), Kasten et al. (1987), and Hess et al. (1990) of the phase diagrams of solid solutions of the lanthanide vanadates and phosphates, were described in much the same way. However, the physical meaning of the fitting parameters used, i.e. characteristics of the random field distribution, which depend on the concentration of mixed components, remained uncertain.

One of the most complicated problems of the solid solution theory is the determination of the distribution function for random fields. In the case of a small concentration pof impurity centers, Ivanov et al. (1983) have obtained the normal distribution for independent random variables Δ_{α} specifying the spectra of the matrix R-ions,

$$g(\Delta_{\alpha}) = \prod_{\alpha} \left(2\pi p \Gamma_{\alpha}^{2}\right)^{-1/2} \exp\left[-\frac{(\Delta_{\alpha} - p\delta_{\alpha})^{2}}{2p \Gamma_{\alpha}^{2}}\right],$$
(285)

with the parameters

$$\delta_{\alpha} = \sum_{m} \Delta_{\alpha}(r_{m}), \qquad \Gamma_{\alpha}^{2} = \sum_{m} \Delta_{\alpha}^{2}(r_{m});$$
where the summation is over all R-ion sites, r_m being the distance of a site from an isolated impurity ion R'. An assumption on the additivity of lattice deformations, induced by separate impurity ions, has been used to derive eq. (285). Obviously, this assumption is not valid if intervals between impurity ions are of the order of the lattice constant. However, it makes it possible to describe effects of the random crystal field in the region of small concentrations (p or 1-p) of one component of the solid solution without any fitting parameters.

The problem of theoretically constructing the phase diagram reduces to the calculation of

- (1) the lattice deformation due to the isolated impurity ion;
- (2) the changes of crystal field parameters, induced by local deformation, for lanthanide ions in different positions with respect to an impurity ion;
- (3) the distribution function of spectral parameters;
- (4) the parameters of the self-consistent field;
- (5) the solution of self-consistent field equations, which are derived by minimizing the free energy, averaged with the distribution function of the single-ion spectral parameters.

Since the crystal field on the lanthanide ions is formed mainly by their nearest surroundings, the elastic-continuum approximation, used by Ivanov et al. (1983) for the description of the lattice deformations induced by a point defect, might result in qualitatively incorrect results when calculating the random component of a crystal field, especially if there are quasimolecular complexes in the lattice.

Malkin et al. (1993) have plotted the phase diagrams for solid solutions of thulium, terbium, and dysprosium vanadates $R_p R'_{1-p} VO_4$, undergoing the low-temperature structural phase transitions. The pseudospin technique has been used. Considering only the lower set of states of Tm³⁺ (non-Kramers doublet), Dy³⁺ (two close Kramers doublets), and Tb³⁺ (singlet-doublet-singlet) ions in the corresponding vanadates (see table 5), the effective Hamiltonian of the R-ions may be presented in the self-consistent field approximation as follows (see eq. 79):

$$\mathcal{H}_{\mathrm{R, eff}} = \left[\Delta(\mathrm{R}) + \Delta_{z}^{\mathrm{R}}\right] \sigma_{z}^{\mathrm{R}} + \Delta_{x}^{\mathrm{R}} \sigma_{x}^{\mathrm{R}} + \Delta_{y}^{\mathrm{R}} \sigma_{y}^{\mathrm{R}} - \sum_{\alpha = x, y} \left[p \lambda_{\mathrm{RR}}^{\alpha} \left\langle \sigma_{\alpha}^{\mathrm{R}} \right\rangle + (1 - p) \lambda_{\mathrm{RR}'}^{\alpha} \left\langle \sigma_{\alpha}^{\mathrm{R}'} \right\rangle \right] \sigma_{\alpha}^{\mathrm{R}},$$
(286)

where only interactions of lanthanide ions with deformations of the A_g, B_{1g} and B_{2g} symmetry are taken into account. The values $\Delta(R)$ (initial splittings) determine ionic spectra in a regular lattice in the high-temperature tetragonal phase, $\Delta(Tm)=0$, $\Delta(Dy)=4.5$, and $\Delta(Tb)=9 \text{ cm}^{-1}$; $\lambda_{RR'}^x$ and $\lambda_{RR'}^y$ are the mean-field constants, responsible for interactions of electronic multipoles of B_{1g}- and B_{2g}-symmetry, respectively, σ_{R}^a are

i	Ion	n _i ^b	R _i	R_i (nm)	$\delta_i \times 10^3$ (nm)	Impurity ion
1	0	4	$(\frac{1}{2}-u, 0, v-\frac{1}{4})$	0.2262	(3.79, 0, -1.50)	Tb ³⁺
			2		(-1.53, 0, 0.60)	Lu ³⁺
2	0	4	(0, u, v)	0.2426	(0, 0.99, 2.97)	Tb ³⁺
					(0, -0.36, -1.12)	Lu ³⁺
3	V	2	$(0, 0, \frac{1}{2})$	0.3129	(0, 0, 1.68)	Tb ³⁺
					(0, 0, -0.65)	Lu ³⁺
4	V	4	$(\frac{1}{2}, 0, \frac{1}{4})$	0.38654	(3.15, 0, -0.69)	Tb ³⁺
					(-1.26, 0, 0.27)	Lu ³⁺
5	Tm	4	$(0, \frac{1}{2}, \frac{1}{4})$	0.38654	(0, 0.04, 0.88)	Tb ³⁺
					(0,-0.02, -0.34)	Lu ³⁺
5	0	8	$(\frac{1}{2} - u, \frac{1}{2}, \frac{1}{2} - v)$	0.43120	(0.24, -0.47, 0.43)	Tb ³⁺
					(-0.10, 0.18, -0.17)	Lu ³⁺
7	0	4	(u, 0, 1-v)	0.44265	(0.24, 0, 0.93)	Tb ³⁺
					(-0.09, 0, -0.36)	Lu ³⁺
3	0	8	$(\frac{1}{2}, u, \frac{3}{4} - v)$	0.46170	(1.11, -0.22, -0.46)	Tb ³⁺
					(-0.44, 0.09, 0.18)	Lu ³⁺
)	0	4	$(\frac{1}{2}+u, 0, v-\frac{1}{4})$	0.48793	(2.34, 0, -1.70)	Tb ³⁺
			1		(-0.95, 0, 0.68)	Lu ³⁺

Table 27 Displacements of host ions from regular positions in the TmVO₄ crystal near impurity Tb^{3+} and Lu^{3+} ions^a

^a Ionic coordinates are given in units of lattice constants (see sect. 1).

^b n_i is the number of ions in the *i*-th coordination shell.

the single-ion operators equal to the Pauli matrices for Tm^{3+} and Dy^{3+} ions in the absence of an applied magnetic field. For Tb^{3+} ions

The projections of operators of lanthanide ion interaction with the random crystal field on the space of the selected states are presented by the parameters Δ_{α}^{R} . The widths of distributions of random variables Δ_{α}^{R} have been calculated using the results of theoretical investigation (Aminov et al. 1990b) of distortions of the crystal structure and the corresponding changes in the crystal field affecting the Tm³⁺ ions near Tb³⁺ and Lu³⁺ impurity ions in the TmVO₄ crystal [the mean values of Δ_{x}^{R} and Δ_{y}^{R} , given by parameters δ_{x} and δ_{y} in eq. (285), equal zero due to their symmetry properties]. The procedure of calculating displacements for 82 ions, surrounding the impurity ion, is described in sect. 3.5; the results are partly given in table 27. The main peculiarity of the



Fig. 37. Fragment of the lattice structure of the $TmVO_4$:Tb crystal. The ion numbers correspond to the coordination shell numbers from table 27.

local deformations in impure vanadate crystals is the relatively considerable displacements of oxygen ions of the ninth coordination sphere of the defect site, which are comparable to the ligand displacements (see fig. 37). This property is due to the rigid bonds in the $(VO_4)^{3-}$ complex. As a result, oxygen ions of the ninth coordination sphere strongly perturb the spectra of neighbouring lanthanide ions in (± 100) , (0 ± 10) sites.

The deviations of rhombic components of the crystal field for the Tm^{3+} ions in different positions relative to the Tb³⁺ impurity ion and the corresponding splittings of the ground doublet are given in table 28. It is seen, that deviations of the crystal field parameters and resulting splittings are essentially non-monotonous functions of the distance to the impurity center. Besides, an essential difference of parameters, determining the random field components of different symmetry, should be noted. This difference predetermines the essentially greater width of the distribution $g(\Delta_x^R)$ in comparison to that of $g(\Delta_y^R)$. It should also be noted that the effects of the random crystal fields of equal strength but of various symmetry on the low-lying energy levels of the Tm³⁺, Dy³⁺, and Tb³⁺ ions are strikingly different. The Dy³⁺ ions interact mainly with the strains of the B_{1g} symmetry, the ground singlet of the Tb³⁺ ions can be connected with the excited singlet by the strains of the B_{2g} symmetry only, and for the Tm³⁺ ions both types of strains are of equal importance. The calculated widths of the random splitting distributions for the Tm³⁺, Dy³⁺, and Tb³⁺ ions in solid solutions of different composition are given in table 29.

We do not present the mean shifts δ_z and dispersion Γ_z of the initial splittings $\Delta(R)$ since their effect on the transition temperatures appears negligible (in particular, $\delta_z = 0.8 \text{ cm}^{-1}$ in the Dy_pGd_{1-p}VO₄ crystal).

The distribution function for the random variables in question being determined, one is in a position to make a step further and to calculate parameters of the self-consistent field of electron multipoles. Equation (285) is obtained as a result of configurational averaging, and parameters $\lambda_{RR'}^{\alpha}$ determine the energy of the R ion in the field of a regular lattice

pq	Positions of Tm ³⁺ ions								
	$\frac{(0, \frac{1}{2}, \frac{1}{4})}{R*=0.387^{a}}$	$(\frac{1}{2}, 0, \frac{3}{4})$ R*=0.588	$\frac{(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})}{R*=0.590}$	(0, 0, 1) R*=0.626	(1, 0, 0) R*=0.707	$(1, \frac{1}{2}, \frac{1}{4})$ R*=0.806			
22	-21.5	9.26	7.29	5.44	31.9	2.46			
42	-3.70	-0.36	-2.58	5.01	-14.9	-0.14			
62	-4.03	3.42	0.19	2.52	2.9	-0.55			
66	-8.12	3.48	3.60	0.29	17.3	1.00			
2–2	0	0	-5.39	0	0	0.63			
4–2	0	0	1.59	0	0	-0.08			
6–2	0	0	0.12	0	0	0.02			
66	0	0	-6.06	0	0	0.54			
ΔE	3.15	1.21	2.07	0.75	4.31	0.40			

Table 28 Parameters ΔB_p^q of the crystal field components of B₁- and B₂-symmetry in the TmVO₄:Tb³⁺ crystal and the splitting ΔE of Tm³⁺ ground doublet (in cm⁻¹)

^a R* is the distance between the Tb³⁺ impurity ion, placed in the center of the coordinate system, and the Tm³⁺ ion (in nm).

 Table 29

 Dispersion of lanthanide ion splittings in mixed crystals with zircon structure

Crystal	Ion	<i>Г</i> _x (К)	<i>Г_у</i> (К)
(DyY)VO ₄	Dy	9.50	0.03
(DyGd)VO₄	Dy	21.8	0.10
Dy(AsV)O ₄	Dy	42.0	0.33
(TmLu)VO ₄	Tm	3.28	1.49
(TmTb)VO4	Tm	8.22	3.75
	Tb	1.40	6.55
(DyTb)VO4	Tb	0.36	1.77
	Dy	9.75	0.02

containing only R' ions. Using conditions (83) and (84) of the free energy minimum, one obtains linear relations between the parameters of lattice deformations $[e_{\alpha\beta}, w_{\alpha}(\lambda)]$ and the mean values of operators $\langle \sigma_{\alpha}^{R} \rangle$. The constants of the effective interionic interaction in the case of ferrodisplacive ordering take the form

$$\lambda_{RR'}^{\alpha} = \frac{n}{\nu C_{\alpha}} B_{\alpha}^{R} B_{\alpha}^{R'} + n \sum_{j_{g}} \frac{B_{\alpha}^{R} (1|0j_{g}) B_{\alpha}^{R'} (1|0j_{g})}{\omega_{j_{g}}(0)^{2}} + \eta_{RR'}^{\alpha},$$
(288)

where n=2 is the number of R-sites in a unit cell of the RVO₄ crystal; $C_x = C(B_{1g})$, $C_y = C(B_{2g})$ are the elastic constants in the absence of any Jahn-Teller coupling (see

R′	$\lambda^{x}_{RR'}(B_{1g})$			$\lambda_{BB'}^{y}(B_{2p})$			
	Tm	Dy	Tb	Tm	Dy	ТЪ	
Tm	0.70	-3.55	-0.22	2.27	-0.47	9.07	
Dy	-3.55	27.8	0.84	-0.47	0.09	-1.80	
ГЪ	-0.22	0.84	0.09	9.07	-1.80	34.35	

 Table 30

 Self-consistent field constants in the lanthanide vanadates (in units of K)

tables 8 and 12). The values B_{α}^{R} , $B_{\alpha}^{R}(1|0j_{g})$ represent the projections of operators of the R-ion interaction with the macroscopic deformations and even optical phonons of the Brillouin zone center, respectively, on the subspace of the selected states of an R ion. Only the deformations and phonons of B_{1g} ($\alpha = x$) and B_{2g} ($\alpha = y$) symmetry are considered. In particular,

$$B_{y}^{\mathrm{Tm}} = \langle \mathrm{Tm} + | \sum_{pq} B_{p}^{(r)q}(\mathrm{B}_{2g}) O_{p}^{q} | \mathrm{Tm} - \rangle ,$$

where the renormalized coupling constants $B_p^{(r)q}$ are defined in eq. (113) and $|\text{Tm}\pm\rangle$ are the wave functions of the ground doublet Γ_5 of the Tm^{3+} ion in a crystal field of the D_{2d} symmetry. Constants $\eta_{RR'}^{\alpha}$ are the corresponding projections of operators $O:\eta(B_{1g}):O$ and $O:\eta(B_{2g}):O$ (see eqs. 142, 143) on the states of R and R' ions (according to definitions 142 and 288 $\lambda_{RR'}^{\alpha} = \lambda_{R'R}^{\alpha}$). For example,

$$\eta_{\mathrm{Tm,Dy}}^{y} = \sum_{pp'qq'} \langle \mathrm{Tm} + | O_{p}^{q} | \mathrm{Tm} - \rangle \eta_{pp'}^{qq'}(\mathrm{B}_{2g}) \langle \mathrm{Dy}\Gamma_{8} | O_{p'}^{q'} | \mathrm{Dy}\Gamma_{6} \rangle, \qquad (289)$$

where $|Dy\Gamma_6\rangle$, $|Dy\Gamma_8\rangle$ are the wave functions of the two lower doublets of Dy^{3+} ions (see table 5). The results of calculations of constants $\lambda^{\alpha}_{RR'}$, performed with the piezospectroscopic measurement data (see table 9) and the estimates of electron-phonon interaction constants within the framework of the exchange charge model, are given in table 30.

The next step in drawing up the phase diagrams is the derivation of the self-consistent field equations. The free energy of the solid solution can be written in the form (cf. eq. 75)

$$F = \frac{n}{2} \sum_{\alpha=x,y} \sum_{\mathbf{RR}'} c_{\mathbf{R}} c_{\mathbf{R}'} \left\langle \sigma_{\alpha}^{\mathbf{R}} \right\rangle \lambda_{\mathbf{RR}'}^{\alpha} \left\langle \sigma_{\alpha}^{\mathbf{R}'} \right\rangle + n \sum_{\mathbf{R}} c_{\mathbf{R}} f_{\mathbf{R}},$$
(290)

where c_R is the concentration of R-type ions ($c_R = p$ or 1-p) and f_R is the averaged single ion free energy

$$f_{\rm R} = -k_{\rm B}T \int \ln\left[\operatorname{Sp}\exp\left(-\frac{\mathcal{H}_{\rm R,\,eff}}{k_{\rm B}T}\right)\right] g_{\rm R}(\Delta_{\alpha}^{\rm R}) \,\mathrm{d}\Delta_{x}^{\rm R} \,\mathrm{d}\Delta_{y}^{\rm R}.$$
(291)

Equations for order parameters $\langle \sigma_{\alpha}^{R} \rangle$ are obtained by minimizing the free energy, $\partial F / \partial \langle \sigma_{\alpha}^{R} \rangle = 0$. When the temperature of a system approaches the transition tempera-

ture $T_D(p)$, it is possible to linearize the self-consistent field equation in $\langle \sigma_a^R \rangle$. From the condition for the existence of non-trivial solutions for these equations we obtain the following equation in relation to the transition temperature:

$$\det \left| \delta_{\mathrm{RR}'} - A^{\alpha}_{\mathrm{R}}(T^{\alpha}_{\mathrm{D}}) \lambda^{\alpha}_{\mathrm{RR}'} c_{\mathrm{R}'} \right| = 0.$$
⁽²⁹²⁾

For crystals containing Tm^{3+} and Dy^{3+} ions

$$A_{\rm R}^{\alpha}(T_{\rm D}) = \int \frac{1}{\varepsilon} \left\{ \tanh\left(\frac{\varepsilon}{k_{\rm B}T}\right) - \left(\frac{\Delta_{\alpha}^{\rm R}}{\varepsilon}\right)^2 \left[\tanh\left(\frac{\varepsilon}{k_{\rm B}T}\right) - \frac{\varepsilon}{k_{\rm B}T\cosh^2\left(\frac{\varepsilon}{k_{\rm B}T}\right)} \right] \right\} \\ \times g_{\rm R}(\Delta_x^{\rm R}, \Delta_y^{\rm R}) \, \mathrm{d}\Delta_x^{\rm R} \, \mathrm{d}\Delta_y^{\rm R},$$
(293)

and

$$\varepsilon = \left[\Delta(\mathbf{R})^2 + \left(\Delta_x^{\mathbf{R}} \right)^2 + \left(\Delta_y^{\mathbf{R}} \right)^2 \right]^{1/2}.$$

For crystals with Tb³⁺ ions

$$A_{Tb}^{x} = \int g_{Tb} d\Delta_{x}^{Tb} d\Delta_{y}^{Tb} \frac{1}{Z} \Biggl\{ \frac{\Delta^{2}(Tb)}{a^{3}} \sinh \frac{a}{k_{B}T} + \frac{(\Delta_{y}^{Tb})^{2}}{b^{3}} \sinh \frac{b}{k_{B}T} + \frac{(\Delta_{x}^{Tb})^{2}}{k_{B}Ta^{2}b^{2}Z} \Biggl[a^{2} + b^{2} + \frac{1}{2}(a-b)^{2} \cosh \frac{a+b}{k_{B}T} + \frac{1}{2}(a+b)^{2} \cosh \frac{a-b}{k_{B}T} \Biggr] \Biggr\},$$
(294)

$$A_{\rm Tb}^{y} = \int g_{\rm Tb} \, dA_{x}^{\rm Tb} \, dA_{y}^{\rm Tb} \times \frac{1}{Z} \left[\frac{(A_{x}^{\rm Tb})^{2}}{b^{3}} \sinh \frac{b}{k_{\rm B}T} + \frac{(A_{y}^{\rm Tb})^{2}}{b^{2}k_{\rm B}TZ} \left(1 + \cosh \frac{a}{k_{\rm B}T} \cosh \frac{b}{k_{\rm B}T} \right) \right],$$
(295)

where

$$a = \left[\Delta(\mathrm{Tb})^2 + (\Delta_x^{\mathrm{Tb}})^2\right]^{1/2}, \qquad b = \left[(\Delta_x^{\mathrm{Tb}})^2 + (\Delta_y^{\mathrm{Tb}})^2\right]^{1/2},$$
$$Z = \cosh\left(\frac{a}{k_{\mathrm{B}}T}\right) + \cosh\left(\frac{b}{k_{\mathrm{B}}T}\right).$$

Phase diagrams for a number of solid solutions $R_p R'_{1-p} VO_4$, $R(M_p M'_{1-p})O_4$, obtained with numerical solution of eq. (292), are given in figs. 38–40.

The present theory gives independent estimates of the ordering temperatures $T_D^{(\alpha)}$ of electron multipoles with B_{1g} and B_{2g} symmetry. The higher one of the two calculated



Fig. 38. Phase diagram for $\text{Tm}_p \text{Lu}_{1-p} \text{VO}_4$ crystals. Measured critical temperatures (*) are from Gehring et al. (1976b), the solid line is obtained from eq. (292).

Fig. 39. Phase diagram for $Dy_p Tb_{1-p}VO_4$ crystals. The solid curves correspond to the solutions of eq. (292). The measured ordering temperatures of the deformations of B_{1g} and B_{2g} symmetry are shown by open and solid circles, respectively (Hess et al. 1990, Vasil'ev et al. 1989, Sokolov et al. 1992b).

temperatures $T_D^{(x)}$ and $T_D^{(y)}$ corresponds to the real phase transition. The temperatures of the structural ordering in the pure TmVO₄, TbVO₄ compounds calculated with the constants $\lambda_{RR'}^{\alpha}$ from table 30 agree with the data of measurements. The value of λ_{DyDy}^{x} gives the mean field transition temperature in the DyVO₄ crystal nearly twice the measured $T_D^{(x)}$. The latter is about 40% lower than expected from the interaction strength indicated by the low-temperature separation of the doublets and it has been known for a long time that the simple mean field approximation is not suitable in this case due to the short range effects. However, as may be seen in figs. 39 and 40, the theoretical $D_{4h}^{19}-D_{2h}^{28}$ phase boundaries obtained without any fitting parameters come closer to the experimental data (the dashed curves in figs. 39 and 40) with the dilution in the dysprosium sublattice because of the rapid diminishing of the short-range interactions.



Fig. 40. Temperatures of the structural (open circles) and antiferromagnetic (solid circles) ordering of $Dy_p Gd_{1-p} VO_4$ crystals (Bingham et al. 1984b). The solid curves represent the results of calculations of $T_D(p)$ (1) and $T_N(p)$ (2, 3) with (1,3) and without (2), taking into account the random strain effects.

The most pronounced effects of the random crystal fields might be expected when the corresponding mean square splittings Γ_{α} are comparable with (or exceed) the energy of ordering in the regular compound $k_{\rm B}T_{\rm D}$. As may be seen in table 29, this condition is satisfied in the Tm_pLu_{1-p}VO₄ system and, in spite of small mismatch of the ionic radii of the Tm^{3+} and Lu^{3+} ions, the theory gives the rapid depression of the ordering temperature in agreement with the measurements (fig. 38). On the contrary, though the dispersion of splittings in the energy spectra of the Tb^{3+} ions is essentially larger than in the spectra of the Tm³⁺ ions (see table 29), it is much less than k_BT_D in TbVO₄, and the phase boundaries of the $D_{4h}^{19}-D_{2h}^{24}$ transitions in the terbium compounds $Tb_pYb_{1-p}VO_4$ (Pilawa et al. 1988), $Tb_pGd_{1-p}VO_4$ (Harley et al. 1974, Glynn et al. 1977), $Tm_pTb_{1-p}VO_4$ (Pilawa et al. 1988), $Tb_pDy_{1-p}VO_4$ (Hess et al. 1990, Sokolov et al. 1992b), differ insignificantly. The widths of the distribution functions of the dysprosium random splittings in $Y_p Dy_{1-p} VO_4$ and $Tb_p Dy_{1-p} VO_4$ are nearly equal (see table 29, the corresponding differences between the ionic radii are equal to 0.0015-0.0010 nm), and the phase diagrams D_{4b}^{19} - D_{2b}^{28} of these systems are very similar with nearly the same limiting concentration $1-p_c = 0.4$ of the Dy³⁺ ions. The difference between the ionic radii of the Gd³⁺ and Dy³⁺ ions is equal 0.003 nm, the dispersion of splittings in the diluted $Gd_p Dy_{1-p} VO_4$ crystal exceeds that in $Tb_p Dy_{1-p} VO_4$ more than twice (see table 29). The curve of the transition points is suppressed remarkably stronger in the former crystal with the critical dysprosium concentration $1-p_c = 0.69$ (see fig. 40, Bingham et al. 1984b). It was shown by different experiments (including measurements of the magnetic susceptibility and X-ray diffraction (Hess et al. 1990, Vasil'ev et al. 1989) that in the mixed $Tb_p Dy_{1-p} VO_4$ crystal there is a range of concentrations in which a monoclinic phase occurs with the coexistence of structural ordering for both B_{1g} and B_{2g} orthorhombic symmetries. The existence of the two structural phase transitions and of a mixed phase appears to be a result of the weak interaction of the Dy³⁺ ions with the B_{2g} strains and of the Tb³⁺ ions with the B_{1g} strains. As one can see in fig. 39, the theory predicts the possibility of observing three phase transitions in $Tb_p Dy_{1-p} VO_4$ at



Fig. 41. Critical temperature $T_{\rm C}(p)$ (crosses, Mennenga et al. 1985, Folkins et al. 1982), and effective susceptibility exponent $\gamma(p)$ (asterisks, Beauvillain et al. 1983) vs. magnetic ion concentration in LiTb_pY_{1-p}F₄. The solid line corresponds to eq. (296).

some concentrations. The effects of the external magnetic field on the phase boundaries in Tb_pDy_{1-p}VO₄ were considered by Sokolov et al. (1992b) in the framework of the pseudo-spin formalism. It was shown that a magnetic field directed in the basal plane of the lattice broadens the range of the existence of the mixed phase and can change the type of the structural ordering. The presented theory needs a further development in the range of concentrations $p \approx 0.5$ when the widths of the distribution functions (285) may be weakly dependent on p.

Now we turn to the discussion of magnetic ordering in the mixed and diluted lanthanide compounds, where in many cases there is a delicate balance between competing shortrange exchange and long-range dipolar interactions. Some attempts to find specific universal random critical behaviour of the diluted uniaxial dipolar ferromagnets appeared unsuccessful. Unlike the critical behaviour of the pure system (see sect. 4.2) the parallel critical susceptibility of the diluted $\text{LiTb}_p Y_{1-p} F_4$ crystals measured by Beauvillain et al. (1983), Brierley and Griffin (1982) in the reduced temperature range $10^{-3} < t < 10^{-1}$ was found to obey the usual power law (218). However there had to exist a nonuniversal concentration-dependent critical exponent $\gamma(p)$ (see fig. 41), which increased with dilution and could be interpreted by a reduction of the effective dimensionality of the diluted system. A similar increase of $\gamma(p)$ was found by Reza and Taylor (1992) in DyAs_pV_{1-p}O₄ crystals undergoing structural transitions. The marked difference between critical and multicritical properties of the random antiferromagnet GdAlO₃:2.5%La and those of a pure system was also found by Rohrer et al. (1980).

Youngblood et al. (1982) have measured the excitation spectra of the LiTb_pY_{1-p}F₄ crystals (p = 0.97 and p = 0.38) in the paramagnetic (T = 4 K) and ferromagnetic (T = 0.35 K) phases by means of neutron scattering and emphasized that the mean-field theory adequately described the dependence of $T_{\rm C}$ on p and the excitation spectrum with excitonic sidebands for p = 0.38. Strong quasielastic scattering observed in the paramagnetic phase was supposed to be due to the long-lived ferromagnetic microdomains. Critical temperatures $T_{\rm C}(p)$ were determined in the magnetic susceptibility (Folkins et al. 1982) and specific heat (Mennenga et al. 1985) measurements for 0.15 , and the resultsare presented in fig. 41. It should be noted that due to the rounding of the susceptibilityand due to the anomaly in the specific heat curves with dilution it is difficult to estimatethe onset of long-range magnetic ordering correctly. Apparently, for low values of p thespecific heat behaviour is predetermined by the hyperfine contribution from the Tb nuclei $and by a Schottky contribution due to the singlet-singlet separation <math>\delta$. Assuming the effective coupling scales linearly with concentration p of magnetic ions, one can find the ferromagnetic transition temperature within the mean-field theory from the simple equation

$$\tanh\left(\frac{\delta}{2k_{\rm B}T_{\rm C}(p)}\right) = \frac{1}{p} \tanh\left(\frac{\delta}{2k_{\rm B}T_{\rm C}(0)}\right),\tag{296}$$

(see solid curve in fig. 41). From eq. (296) we have the nonzero critical concentration $p_c = 0.23$, below which no electronic magnetic ordering is to be expected. As may be seen in fig. 41, the experimental data are close to the mean-field results. The effect of random crystal fields due to the Y/Tb mismatch on the Tb quasidoublet is negligible; according to the calculations of local lattice deformations by Aminov et al. (1990b), the alteration of δ near the impure Y ions do not exceed 0.02 cm^{-1} . However, magnetic ordering is still observed from the susceptibility measurements for $p < p_c$. Folkins et al. (1982) suggested that the value $T_C = (0.135 \pm 0.015)$ K for p = 0.15 corresponded to an enhanced nuclear magnetic ordering.

One more system with induced magnetism investigated in the regime of dilution is the hydrated thulium sulfate. In the mean field approximation the interionic coupling constant K_0 is proportional to the concentration p of the magnetic ions (see eqs. 210– 212), and the ratio $R_{\rm e}$ which determines the regime of magnetic ordering may be gradually reduced with dilution. Simizu and Friedberg (1982, 1983) measured heat capacities and the ac magnetic susceptibilities of a series of diluted $(Tm_pY_{1-p})_2(SO_4)_3 \cdot 8H_2O$ crystals between 0.06 and 0.7 K. The pure salt is an antiferromagnet with $T_N = 0.29$ K and the ratio $R_e = 1.112$. Because this value of R_e barely exceeds unity, one might expect the regime of ordering to change from electronic to coupled electron-nuclear. The calculated values of the critical temperatures in the diluted samples, while taking into account the hyperfine interaction, appeared overestimated in comparison with the experimental data. The slow nonlinear decrease of $T_{\rm N}(p)$ after a rapid initial fall was assumed to be a result of the varying ratio between the competitive short-range antiferromagnetic and the dipolar interactions at dilution. The random arrangement of magnetic moments in the dilute crystals can exhibit a wide distribution of local fields with different signs. This could produce a high degree of "frustration" so that the ordered state of such a system might resemble that of a spin glass. The similar problem of identifying the spinglass states in the LiHo_pY_{1-p}F₄ and DyP_pV_{1-p}O₄ crystals (see figs. 42 and 43) was thoroughly investigated by Reich et al. (1986, 1990), Wu et al. (1993), and Dirkmaat et al. (1987). In the LiHo_p $Y_{1-p}F_4$ Ising ferromagnet effects of random strains may be neglected



Fig. 42. Phase diagram for LiHo_p $Y_{1-p}F_4$ Ising magnet. PM, paramagnet; FM, ferromagnet; SG, spin glass. Experimental data are from neutron scattering and magnetic susceptibility measurements (Kjaer et al. 1989, Reich et al. 1990).

Fig. 43. Phase diagram for $DyV_pP_{1-p}O_4$ crystals. PM, paramagnet; AF, antiferromagnet; SG, spin glass. Directions of the Dy^{3+} ion magnetic moment in the different phases are shown. Critical temperatures have been measured by Dirkmaat et al. (1987).

due to a small difference between the ionic radii of the Ho³⁺ and Y³⁺ ions. The Curie temperatures $T_{\rm C}(p)$ obey mean field scaling relative to that of pure LiHoF₄, excepting the range of rather small holmium concentrations (see fig. 42). A theoretical analysis of the random crystal field effects on the magnetic ordering may be performed quite similarly to that described above. For example, in the case of the Kramers ions the *g*-factors of the ground doublet are random variables. It is possible to calculate the parameters of the corresponding distribution functions (285) with the crystal field perturbations induced by the impurity ions. Malkin et al. (1993) obtained much better agreement with the experimental data when taking into account the random variations of the *g*-factors of the Dy³⁺ ions in the calculations of the magnetic phase diagram of the mixed Gd_pDy_{1-p}VO₄ crystal (curves 2 and 3 in fig. 40).

Although the pure $DyPO_4$ and $DyVO_4$ crystals are antiferromagnets with the orthogonal easy axes of the magnetization (see sect. 4.2) the mixed $DyP_pV_{1-p}O_4$ crystals belong to the class of random anisotropy systems. Due to the large mismatch P/V (displacements of the nearest neighbours of the impurity ion exceed 0.01 nm) the dysprosium ions are affected by the highly inhomogeneous crystal field, and the spin anisotropies are in size and direction, randomly distributed over a large number of discrete possibilities. The phase diagram of this system obtained by Dirkmaat et al. (1987) in a systematic experimental study of the ac susceptibility (see fig. 43) displays some remarkable features. At both extremes of p (0 and 1) a very strong decrease of the Néel temperature was found, indicating that the long range antiferromagnetic order was strongly affected by the admixture of the minority component. No longrange magnetic order had been detected at intermediate concentrations (0.3and for all concentrations when measured perpendicular to the easy axis. Spin-glasslike properties were observed at the temperatures $T < T_{\rm f}$ (the temperatures at which the maxima in the real part of the ac susceptibility occur are defined as the freezing temperatures $T_{\rm f}$). The concentration dependence of the freezing temperature is extremely weak but at both ends of the phase diagram $T_{\rm f}$ appears to bend towards zero.

It should be noted that the data on the relaxation rates and spin dynamics of the diluted and mixed LiHo_pY_{1-p}F₄ (Reich et al. 1990), LiTb_pY_{1-p}F₄ (Lloyd and Mitchell 1990) and DyP_pV_{1-p}O₄ (Dirkmaat et al. 1987), obtained in the frequency dependent ac susceptibility measurements and in the inelastic neutron scattering experiments, demand special discussion.

6. Rare earths in RBa₂Cu₃O_{6+x} compounds

6.1. Crystal structure and mesoscopic phase separation

RBa₂Cu₃O_{6+x} compounds, known for their superconducting properties, possess certain peculiarities which appear to be of a great interest for the physics of rare earths. First, this system can be considered to a certain extent as a two-dimensional one, since the distance between R ions along the *c*-axis is three times larger than that in the *ab*-plane. Being located just between the principal CuO₂ planes, R ions seem to be excellent probes for basic studies of 2D-effects in both antiferromagnetism and (super)conductivity. Second, at intermediate oxygen contents the highly disordered oxygen "lattice" coexists with the rigid crystal lattice of heavy atoms (R, Ba, Cu), giving rise to the glassy-like properties of the whole system. Using a rather high mobility of oxygen atoms in the CuO_x basal planes, one can easily influence the effects of the local oxygen ordering and produce a wide variety of metastable states intermediate between the crystalline and glassy ones. The RBa₂Cu₃O_{6+x} compounds can be regarded as a solid solution of oxygen in the tetragonal RBa₂Cu₃O₆ lattice. Their structure is shown in fig. 44 (Jorgensen et al. 1990a). At x < 0.4, oxygen atoms occupy O(1) and O(5) positions with equal probability, so that the structure remains tetragonal (T). At x > 0.4, oxygen ordering occurs in the CuO_x planes: O(1) positions become preferable and the Cu–O–···–O–Cu chain



Fig. 44. Crystal structure of the RBa₂Cu₃O_{6+x} compounds.



Fig. 45. Critical temperatures and superconducting volume fractions in YBa₂Cu₃O_{6+x} and TmBa₂Cu₃O_{6+x}. (a) Critical temperatures: triangles and squares for YBa₂Cu₃O_{6+x} at the midpoint of the superconducting transition (Graf et al. 1990); solid circles for TmBa₂Cu₃O_{6+x} at the onset of the transition (Bakharev et al. 1994). (b) Superconducting volume fractions: triangles and squares for YBa₂Cu₃O_{6+x} (Graf et al. 1990); solid circles for TmBa₂Cu₃O_{6+x} (Bakharev et al. 1994); stars indicate results from the Gd³⁺ EPR intensity (Pekker et al. 1991, Rockenbauer et al. 1992, see eq. 300).

NONMETALLIC LANTHANIDE COMPOUNDS

x	<i>T</i> _c (K)	a (Å)	b (Å)	c (Å)
0.98(6)	94	3.857(1)	3.912(1)	11.722(1)
0.98(8)	94	3.849(1)	3.898(1)	11.691(1)
0.98(8)	94	3.818(1)	3.884(1)	11.649(1)
1.00(6)	90	3.817(1)	3.883(1)	11.633(1)
1.02(6)	93	3.818(1)	3.883(1)	11.633(1)
1.02(6)	91	3.814(1)	3.879(1)	11.629(1)
1.01(6)	90	3.801(1)	3.871(1)	11.616(1)
0.99(6)	90	3.796(1)	3.866(1)	11.613(1)
	x 0.98(6) 0.98(8) 0.98(8) 1.00(6) 1.02(6) 1.02(6) 1.01(6) 0.99(6)	x T_{c} (K) 0.98(6) 94 0.98(8) 94 0.98(8) 94 1.00(6) 90 1.02(6) 93 1.01(6) 90 0.99(6) 90	x T_c (K)a (Å)0.98(6)943.857(1)0.98(8)943.849(1)0.98(8)943.818(1)1.00(6)903.817(1)1.02(6)933.818(1)1.02(6)913.814(1)1.01(6)903.801(1)0.99(6)903.796(1)	x T_c (K)a (Å)b (Å)0.98(6)943.857(1)3.912(1)0.98(8)943.849(1)3.898(1)0.98(8)943.818(1)3.884(1)1.00(6)903.817(1)3.883(1)1.02(6)933.818(1)3.883(1)1.02(6)913.814(1)3.879(1)1.01(6)903.801(1)3.871(1)0.99(6)903.796(1)3.866(1)

 Table 31

 Lattice parameters and critical temperatures of RBa₂Cu₃O_{6+x} compounds (Guillaume et al. 1993)

fragments begin to order in the *b*-direction, the *b* lattice parameter increasing, *a* and *c* parameters decreasing, and the crystal lattice becoming orthorhombic (O). The T--O transition is accompanied by current carriers appearing in the CuO₂ planes, and the compound becomes a superconductor at temperatures below $T_c(x)$. Typical dependencies of critical temperature and Meissner fraction on oxygen index 6+x for YBa₂Cu₃O_{6+x} are shown in fig. 45 (Graf et al. 1990). Full substitution of yttrium by R ions Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, and Yb changes the superconducting properties very little (see table 31), and only three compounds of this series (CeBaCuO, PrBaCuO and TbBaCuO) are not superconducting.

Two typical "plateaus" on the $T_c(x)$ curve are associated with two main ordered structures. For one of them, called "Ortho I", all CuO chains are occupied by the oxygen atoms and the critical temperature is close to 90 K. In the "Ortho II" phase with the critical temperature near 60K, "full" and "empty" chains alternate, forming the superstructure with a double lattice period 2a. A number of papers is devoted to the problem of oxygen ordering in 1-2-3 systems (e.g., Fontaine et al. 1987, 1990, Khachaturyan and Morris 1987, Aligia et al. 1988, Kikuchi and Choi 1989, Sterne and Wille 1989). It was shown that at any oxygen content x > 0.4, the crystal heated to a temperature higher than 700°C has the tetragonal symmetry, because a high oxygen diffusion rate makes O(1) and O(5) sites indistinguishable. A computer simulation (Semenovskaya and Khachaturyan 1992) of 2D-diffusion of interacting oxygen atoms, taking place in the CuO_x plane when cooling a sample, gives a complicated sequence of structural transformations of a mesoscopic scale, including the "primary tweed OI" structure (fig. 46a), the "secondary tweed OII" structure (fig. 46b), and the "glass-like phase" (fig. 46c). The latter two structural states (figs. 46b,c) are regarded as mesoscopic phases, i.e., such metastable (or stable) phases, the typical structural peculiarities of which are determined not so much on atomic scale usual for regular crystals, but on mesoscopic scale. At an oxygen concentration $0.5 < x \le 0.88$, the final mesostructure does not depend on the cooling conditions: both at slow cooling and



Fig. 46. Simulated microstructures of the CuO_x layers in the YBa₂Cu₃O_{6+x} compounds (Semenovskaya and Khachaturyan 1992): a, b, tweed pattern formation in YBa₂Cu₃O_{6,5} produced by the isothermal annealing T phase at ~500 K; a, primary tweed consisting of OI domains, the annealing time $t = 1.2 \tau$, where τ is the jump time for the oxygen diffusion; b, secondary tweed consisting of OII domains formed from the primary tweed domains (the annealing time $t = 64 \tau$). Small black dots are Cu atoms, and larger dark circles are O atoms. The model crystal consists of 64×64 unit cells. The microstructure (c), obtained by the isothermal homogeneous secondary ordering of a single orientational variant of the OI phase at room temperature, describes the metastable "glassy" phase (short-range ordering of OII-type) consisting of anti-phase OII domains.

quenching, a system of antiphase OII domains is obtained (fig. 46c). It is metastable (or stable), since its development stops in \sim (40–100) τ after cooling begins, τ being the diffusion time for an oxygen atom to move from the O(5) to the O(1) site. At an oxygen concentration close to x=0.5, the final mesostructure is the "secondary tweed OII" (fig. 46b). This structure is also metastable: the system development stops when its free energy reaches the local minimum, and its further transformation into an ordinary equilibrium OII phase can continue only if the OII seed appears and grows. The oxygen concentration at the structural domain boundaries is reduced; the greater the deviation from stoichiometry (x=1) of the compound, the less the oxygen concentration at the boundaries.

So, the main structural peculiarity of conducting oxygen-deficient 1-2-3 compounds is that together with the regular (i.e., without any vacancies) BaO-CuO₂-R-CuO₂--BaO layers, they contain CuO_x layers built, just like a mosaic, of oxygen-containing "slices" separated by oxygen-deficient boundaries. The size of these "slices" depends in a complicated manner on the oxygen index and on the way the compound is prepared, but they can be present in all compounds without exceptions, including those with x = 1, so that the usual classification of the samples in terms of "bad-good" can hardly be regarded as satisfactory and should be replaced, if possible, by characterization of the evolution stage of a given sample at a given moment.

Different methods are used to characterize the state of a compound. Most well known are electron microscopy (Reyes-Gasga et al. 1989a), electron, neutron and X-ray diffraction (Beyers et al. 1989, Cava et al. 1990, Chrosch and Salje 1994), scanning

tunneling microscopy (Edwards et al. 1992), resonant Raman scattering spectroscopy (Iliev et al. 1993), as well as the resonant methods using some local probes, i.e., EPR (Pekker et al. 1991, Rockenbauer et al. 1992, Kurkin et al. 1993), NMR (Mehring 1992, Heinmaa et al. 1992, Brinkmann and Mali 1994), Mössbauer spectroscopy (Hodges et al. 1991a,b), and inelastic neutron scattering (Furrer et al. 1988, Mesot et al. 1993a). Some of these methods allow an approximate estimate of the sizes of the mesoscopic structure grains – the electron and neutron diffractions (Bevers et al. 1989, Cava et al. 1990), tunneling microscopy and spectroscopy (Edwards et al. 1992), and ultrahigh resolution electron microscopy (Horiuchi 1992). For example, the mean sizes of OIIphase grains, estimated using diffusive neutron scattering (Zeiske et al. 1991), are $10a \times 24b \times 2c$ or $40 \times 90 \times 24$ Å³ for YBa₂Cu₃O_{6+x} at x = 0.4, which gives a visual idea of the real structure of these compounds. For compounds with x=0.4, it was found with the help of ultrahigh resolution microscope, that two phases, orthorhombic (the most part) and pseudotetragonal, coexist in a crystal, the oxygen atoms tending to concentrate in areas with a size less than 100 Å and forming clusters with size varying from 8 to 30 Å (Horiuchi 1992). The experimental data concerning the grain size are corresponding rather well to the calculated ones (fig. 46b).

With oxygen content and low-temperature annealing time increasing the "grains" size in CuO_x planes also increases. For example, for large single crystals $(2 \times 2 \times 0.2 \text{ mm}^3)$ with high critical temperature $(T_c = 92 \text{ K}, \text{ superconducting transition width of 1 K})$ the mean distance between OI domains (twins) is about 200 Å, the domain wall thickness being of 7 ± 2 Å (Chrosch and Salje 1994). It is also possible to obtain single domain samples (Voronkova et al. 1990, Welp et al. 1992), but even in chemically stable crystals containing no twins (for example, YBa₂Cu₄O₈) the electron microscopy together with electron energy loss spectroscopy show the abundance of oxygen-deficient areas (Zhang et al. 1993).

The process of oxygen ordering in non-equilibrium compounds is conventionally supposed to proceed in three stages: the ordering inside the CuO chain fragments, the chains ordering in a two-dimensional periodic structure (for example, of OIItype) and, finally, the CuO_x planes ordering in a three-dimensional periodic structure (Reves-Gasga et al. 1989b). The first stage of this process should be the fastest, since at this stage only oxygen diffusion from the O(5) to the O(1) chain site is needed. The mean time of such diffusion, $\tau_0^{(2)} = r_{51}^2/4D^{(2)}$ (where $r_{51} = a\sqrt{2}$ is the O(5)– O(1) distance, a=3.85 Å is the lattice constant), can be estimated if the diffusion coefficient $D^{(2)} = D_0 \exp(-E_a^{(2)}/k_BT)$ is known. Taking the activation energy $E_a^{(2)}$ equals 1.0 eV (the mean value of 0.97 eV (Rothman et al. 1989, 1991), 0.96 eV (Veal et al. 1990), 0.99 eV (Islam and Baetzold 1994), 1.03 eV (Xie et al. 1989), and 1.07 eV (Tallon and Staines 1990), and using the diffusion coefficients 4×10^{-13} cm²/s (Rothman et al. 1989, 1991), and 1×10^{-12} cm²/s (Krauns and Krebs 1993), measured at 300°C, one finds the D_0 value to range between 2.5×10^{-4} to 6.2×10^{-4} cm²/s, and the mean diffusion time at room temperature to range between 5 and 13 hours. In the neutron diffraction experiments (Jorgensen et al. 1990b), made on the quenched powder of $YBa_2Cu_3O_{6,41}$ compound, it was noticed that during the room temperature annealing the lattice parameters, orthorhombicity and interatomic distances, as well as the critical temperature, change in time according to the law:

$$T_{\rm c}(t) = T_{\rm c}(\infty) - [T_{\rm c}(\infty) - T_{\rm c}(0)] \exp\left(-\sqrt{\frac{t}{\tau_{\rm RT}}}\right)$$
(297)

with the parameter $\tau_{RT} = 386$ minutes. Later experiments by the same authors on a sample with x = 0.45 have shown $\tau_{RT} = 572$ minutes. However, a shorter process was observed in the Raman scattering experiments made on quenched YBa₂Cu₃O_{6.5} single crystals (Hadjiev et al. 1993): it appeared that the 490 cm⁻¹ spectral line shape, which "feels" oxygen ordering in CuO_x planes well enough, stops changing after the first 60 minutes of room-temperature "aging". It is natural to consider this short time (one order of magnitude shorter than that estimated above) to be close to the characteristic $\tau_{RT}^{(2)}$ time of the shortest process at room temperature. If $\tau_{RT}^{(2)} = 0.5$ hour, we will have

$$\tau^{(2)} \text{ (hours)} = 8 \times 10^{-18} \exp\left(\frac{1.0 \text{ eV}}{k_{\text{B}}T}\right).$$
 (298)

If the diffusion time $\tau^{(2)} = r_{51}^2/4D^{(2)}$ characterizes the 2D-ordering in the CuO_x plane, one should also include the existence of a $\tau^{(3)}$ parameter, characterizing the establishment of structure correlation between the adjacent CuO_x planes. The latter process must proceed at rather high temperatures, i.e., at conditions when the oxygen atoms in BaO planes also appear to be mobile (Jorgensen et al. 1990a), therefore the structure correlation between the adjacent CuO_x planes can be established due to double jumps of O(1)–O(4)–O(1) type. The activation energy of one jump is equal to 0.9 eV (Islam and Baetzold 1994), therefore the activation energy of a double jump through the "bridging" oxygen O(4) ($E_a^{(3)} = 1.8 \text{ eV}$) should be less than that for O(1)–O(5)–O(1) jump (2.0 eV), and the parameter $\tau^{(3)}$ of the 3D-ordering is equal to

$$\tau^{(3)} \text{ (hours)} = 8 \times 10^{-18} \exp\left(\frac{1.8 \text{ eV}}{k_{\rm B}T}\right).$$
 (299)

In fig. 47 the temperature dependence of both characteristic times, $\tau^{(2)}$ and $\tau^{(3)}$, is shown. This figure does not pretend to quantitatively describe the oxygen ordering processes, but it allows one to understand the following important peculiarity of oxygen-deficient RBa₂Cu₃O_{6+x} compounds. The temperature $T_{\rm f}$ exists, which separates the ranges of different oxygen dynamics of the 1-2-3 compounds and thus resembles the phase transition temperature. At $T < T_{\rm f}$ a compound looks like a "frozen" system, and at $T > T_{\rm f}$ it has a mobile oxygen sublattice. Visually, the "freezing" temperature $T_{\rm f}$ depends on experiment duration, in which the investigator is able to notice some physical parameters changing due to the oxygen ordering. For instance, if the experiment is running for a time between 1 day and 1 month, the temperature $T_{\rm f}^{(2)}$ can lay between 250 K and 270 K, and



Fig. 47. Temperature dependencies of the jump times $\tau^{(2)}$ and $\tau^{(3)}$ characterizing two-dimensional (in the CuO_x layers only) and three-dimensional (interlayer) oxygen ordering in the YBa₂Cu₃O_{6+x} compounds.

 $T_{\rm f}^{(3)}$ between 460 K and 490 K. The temperature $T_{\rm f}^{(2)}$, corresponding to O(5)–O(1) jump "freezing", was mentioned in the literature (see, for example, Sun et al. 1988, Lavrov 1992, Cannelli et al. 1990, Metzger et al. 1993). We shall not discuss here the long-term processes of forming the two- and three-dimensional OII structures. Their durations depend on a number of factors (Semenovskaya and Khachaturyan 1992): oxygen index, cooling regime, primary "tweed OI" grain size, or the size of twins, etc., thus it is not surprising that a wide variety of relaxation times (297) is obtained in experiments with different samples.

At temperatures below $T_{\rm f}^{(3)}$, the oxygen self-diffusion in the *c*-axis direction is absent $(D_c/D_{ab} \approx 10^{-4}$ even at 400°C (Bredikhin et al. 1991); moreover, the motion of the O(1)-O(4)-O(1) type which helps to establish some partial structural correlation between adjacent CuO_x planes also stops. Therefore, if the sample at the beginning was in equilibrium in the high-temperature tetragonal phase and was then quickly cooled (quenched) to the temperature $T_{\rm f}^{(2)} < T < T_{\rm f}^{(3)}$, the formation of the OII mesoscopic phase (the secondary OII tweed, fig. 46b, or glass-like OII state, fig. 46c) takes place independently in each CuO_x layer. The alternation of oxygen-rich (conducting) and oxygenpoor (nonconducting) layers, forming S-I-S nano-sandwiches at low temperatures, should be the natural consequence of this process. The following arguments can be listed in favour of the existence of isolating layers, perpendicular to the c-axis, in oxygen-deficient 1-2-3 compounds. First, it is reasonable to assume (Phillips 1992) that the structural defects should follow rules similar to those obeyed by the structure itself; in this case the existence of oxygen-deficient layers (lengthy layer structure defects) seems to be quite natural. Second, it follows from experiments on YBCO single crystals (Cooper et al. 1993) that the optical conductivity in the c-axis direction, extrapolated to zero frequency, changes from $200 \,\Omega^{-1} \,\mathrm{cm}^{-1}$ at $x = 1 \,(T_{\rm c} \approx 90 \,\mathrm{K})$ to a value less than $50 \,\Omega^{-1} \,\mathrm{cm}^{-1}$ at x = 0.8 ($T_c = 81$ K) and goes to zero at x = 0.7 ($T_c = 70$ K). Third, the "paramagnetic

Meissner effect" (Braunisch et al. 1992) (or "Wohlleben effect", Sigrist and Rice 1992), ascribed to the orbital currents and observed more often in the layered S-I-S samples, was recently discovered in oxygen-deficient YBa₂Cu₃O_{6+x} single crystals ($x = 0.85 \approx 0.95$) in the magnetic field parallel to the c-axis only (Riedling et al. 1994). This means that spontaneous currents are restricted by the separated conducting copper-oxygen layers. Fourth, the direct measurement of intrinsic Josephson effects in Bi₂Sr₂CaCu₂O₈, $Tl_2Ba_2Cu_3O_{10}$, and $YBa_2Cu_3O_{6+x}$ crystals, using currents flowing along the c-axis had clearly shown (Kleiner and Muller 1994) that these compounds behave as stacks of S-I-S Josephson junctions; the estimates of junction thickness in BSCCO gave a value of about 15 Å. And finally fifth, the superconducting layer stacking model is supported also by recent observations of a dirty-limit-like superconductivity in the c direction in the YBa₂Cu₃O_{6+x} crystal, exhibiting a completely metallic far-infrared c-axis response (Schutzmann et al. 1994). Thus, all known facts and reasoning lead to the conclusion that the oxygen-deficient RBa₂Cu₃O_{6+x} superconductor is a metastable mesoscopic structure of superconducting clusters separated by oxygen-deficient nonconducting layers and boundaries, i.e., the structure of S-I-S nano-sandwiches. The superconductivity in such a system as a whole can be provided only by cluster percolation. In other words, one arrives at the conclusion, already claimed in the first paper on the high- $T_{\rm c}$ superconductivity (Bednorz and Müller 1986), and different versions of which are continuing to be discussed up to this moment (Mesot et al. 1993a, Phillips 1992, Muroi and Street 1993a, b, Deutscher and Müller 1987, Blackstead 1993, Halbritter 1993, Bulaevskii et al. 1992, Claus et al. 1992, Osofsky et al. 1992, Kubo and Igarashi 1989), namely: the layered cuprates are essentially inhomogeneous systems and the superconductivity in them is of a percolative nature.

When preparing the high-quality 1-2-3 superconductors, it is usual to slowly cool the sample saving its chemical composition (Reyes-Gasga et al. 1989b). It is possible in this way to obtain the substance with different oxygen indices containing, besides T- and OI-phases, only one superstructure, i.e., Ortho II; its volume part is determined by x and reaches a maximum at x = 0.6 (Krekels et al. 1992). As one can see in fig. 45b, the volume part of the superconductor V_{sc} reaches a maximum at this x, the main maximum of V_{sc} being at x = 1.0, whereas at x = 0.85 the minimum value of V_{sc} is observed. Such behaviour of $V_{sc}(x)$ curve is naturally explained if one assumes the necessity of structural correlation between CuO_x layers: the probability to satisfy this condition at x = 1.0 and x = 0.5 is higher than at x = 0.8.

The influence of the structural correlation between CuO_x layers on high- T_c superconductivity seems to follow from experiments of Yang et al. (1992), in which the properties of a "good" YBa₂Cu₃O_{6.72} sample, "spoiled" by heating to $T > T_f^{(3)}$, were investigated. Indeed, when annealing this sample at 51°C after "spoiling", two processes with the characteristic times of 20 minutes and 250 hours were found. The first process according to its duration (it would last about 300 minutes at room temperature) is comparable with those observed previously when annealing the quenched samples (Veal et al. 1990, Jorgensen et al. 1990b), so it is natural to associate it with the noncorrelated processes of local ordering (disordering) in CuO_x planes due to the O(5)–O(1) jumps. The O(4) motion

at 51°C should be "frozen", thus the second process should also be associated with the O(5)–O(1) jumps. What does this process look like? Taking into account that it is followed by an increase of T_c , one can conclude that the long-term annealing at $T_f^{(2)} < T < T_f^{(3)}$, results in a partially correlated ordering of the oxygen atoms in adjacent CuO_x layers.

What causes the oxygen atoms in adjacent CuO_x planes to order in chains along the *b*-axis not randomly but correlatively, i.e., to create some 3D-ordered domains in a disordered crystal? In other words, what is the reason for mesoscopic phase separation in RBa₂Cu₃O_{6+x} compounds? Just as in La₂CuO_{4+x} (Vaknin et al. 1994), two scenarios can take place here. In the first, the current carriers (the holes) in the CuO₂ planes are "expelled" from the antiferromagnetic areas and gather in clusters, dragging with them the oxygen atoms in CuO_x planes (Emery et al. 1990, Kivelson et al. 1990, Emery and Kivelson 1993). This process is energetically profitable, because the holes, combined in clusters, destroy fewer antiferromagnetic bonds between the Cu²⁺ ions in the Cu(2) planes, than single holes distributed randomly in these planes. In the second scenario, the system minimizes the elastic energy, gathering in clusters the crystal lattice defects, i.e., O(1) atoms, but not holes.

In 1-2-3 samples subjected to a long-term annealing procedure at low temperatures, the oxygen atoms in separate CuO_x layers are ordered, i.e., they enter into the CuO chain fragments. Hence, one can admit the environment of the R ion to be formed by these Cu(1)-O(1) chain fragment, but not by single O(1) and Cu(1) atoms. This feature has been clearly seen for the first time in the Gd³⁺ EPR spectra of the aligned $Y_{0.999}$ Gd_{0.001}Ba₂Cu₃O_{6+x} powder (Pekker et al. 1991, Rockenbauer et al. 1992). The "fine structure" of the $|+\frac{7}{2}\rangle \leftrightarrow |+\frac{5}{2}\rangle$ line shown in fig. 48 depends strongly on oxygen content. The analysis of such spectra has made it possible to conclude (Pekker et al. 1991, Rockenbauer et al. 1992) that five types of the combinations of "full" and "empty" CuO chains (i.e., K_0 , K_1 , K_2 , K_3 , and K_4), form five types of Gd³⁺-centers in relative amounts consistent with the model of 2D-ordering of the chains in CuO_x layers.

This conclusion was confirmed by the ¹⁶⁹Tm NMR spectra in TmBa₂Cu₃O_{6+x} samples (Lütgemeier et al. 1993). Before the experiments were done, these samples were kept at room temperature for more than a year. It is seen in table 5, that the lowest electron energy level of the Tm^{3+} ion is separated from the excited 4f-states by more than 100 cm^{-1} . therefore the "enhanced NMR" of thulium nuclei can be easily observed at temperatures below ~40 K (Bakharev et al. 1991, 1992a,b, 1993, 1994, 1995a, Teplov et al. 1991, 1994, Egorov et al. 1992, Krjukov et al. 1994). The splitting of the nuclear energy levels in a magnetic field is described by a spin Hamiltonian of a rhombic symmetry, their parameters for the basic three phases (OI, OII, T) are shown in table 32. Using these parameters, as well as measured energies of the lower states of Tm³⁺ ions (Allenspach et al. 1991), one can try to find the parameters of the crystal electric field for all three phases. The results of such attempts (see table 7d) confirm the tendency in the crystal field potential for Er compounds mentioned in sect. 2: the parameters B_{40} , B_{44} , B_{60} , B_{64} do not depend much on x while B_{20} increases more than twice at x increasing from 0 to 1. It should be noted that the crystal field in TmBa₂Cu₄O₈ was found to be strikingly similar to that in $TmBa_2Cu_3O_{6.5}$ (see table 7d).



Fig. 48. Gd^{3+} EPR spectra in $Y_{0.999}Gd_{0.001}Ba_2Cu_3O_{64x}$. (a) Evolution of the $|\frac{7}{2}\rangle \leftrightarrow |\frac{5}{2}\rangle$ transition as a function of the oxygen content x. Spectra were taken at 9.1 GHz in the temperature range 77–92 K. Lines A, B, D, F and G correspond to well-determined CuO chain configurations K_0 , K_1 , K_2 , K_3 and K_4 , respectively. (b) Concentration dependence of the relative amounts of the local CuO chain configurations. Open square, open triangle, asterisk, solid triangle, and solid square, represent the 0, 1, 2, 3 and 4 fold occupied configurations, respectively. The calculated intensities are represented by the solid curves (from Pekker et al. 1991, Rockenbauer et al. 1992).

Table 32 Spin-Hamiltonian parameters of ¹⁶⁹Tm nuclei at liquid helium temperatures in TmBa₂Cu₃O_{6+x} crystals (in kHz/Oe)

x	$ \gamma_a/2\pi $	$ \gamma_b/2\pi $	$ \gamma_c/2\pi $
1.0 (Ortho I)	5.3(1)	6.8(1)	2.20(5)
0.5 (Ortho II)	5.3(1)	6.1(1)	2.56(5)
0.0 (Tetra)	5.3(1)	5.3(1)	3.05(5)



Fig. 49. ¹⁶⁹Tm NMR spectra of TmBa₂Cu₃O_{6.8} aligned powder at 4.2 K (Bakharev et al. 1994); v = 49.7 MHz; pulse sequence = 1.5-20-3.0 µs; pulse repetition frequency is 330 Hz in parts (a) and (c), and 1 Hz in (b). Parameters of the fitting curves in part (b) are: K_4 , $\gamma_c/2\pi = 2.163$ kHz/Oe; K_3 , $\gamma_c/2\pi =$ 2.373 kHz/Oe; K_2 , $\gamma_c/2\pi = 2.560$ kHz/Oe; D, $\gamma_c/2\pi = 2.708$ kHz/Oe (the D-line seems to belong to the disordered structure). Numbers in parentheses denote relative intensities.

Measurement of diamagnetic susceptibility of superconducting TmBa₂Cu₃O_{6+x} compounds in an ac field of 1 Oe (~1 kHz), perpendicular to the *c*-axis of aligned powdered samples, has confirmed (Bakharev et al. 1994) the superconducting volume fraction V_{sc} to have a minimum at x=0.8 (cf. fig. 45b). One can see the resonance K_3 -lines in both the Gd³⁺ EPR spectra at x=0.7, 0.77 and 0.87 (fig. 48a), and the ¹⁶⁹Tm NMR spectra at x=0.8 (fig. 49) in a magnetic field $H_0 || c$. It follows from fig. 48b that the relative amount



Fig. 50. Plausible structural fragments of oxygen-deficient RBa₂Cu₃O_{6+x} compounds (Bakharev et al. 1994).

of K_3 -centers reaches a maximum value at x=0.7-0.8, i.e., just at such oxygen contents, which correspond to the minimum value of the superconducting volume fraction. Taken together, these facts can be interpreted in the following way: the part of the whole volume of the superconducting sample, occupied by a K_3 -center, is not superconducting, i.e., the oxygen-deficient 1-2-3 compounds have the layered S-N-S structure like that in fig. 50.

The inhomogeneous halfwidth of the K_3 -line does not differ much from that of the K_2 and K_4 -lines (see figs. 48a and 49b, c). This gives evidence that the distribution of the K_3 -centers in the crystal lattice is not random, i.e., similar to K_2 - and K_4 -centers; the K_3 centers form, at least, small planar clusters as is shown in fig. 50. In order to be convinced of a correctness of the layered structure in fig. 50, one needs to answer the following important question: why is it necessary for the superconductivity that a pair of CuO_2 layers lies between identical CuO_x layers (of OI- or OII-type), but not between different ones? The answer can be simple: in samples with an oxygen content corresponding to a step between 90K and 60K plateaus, the ordered regions in "filled" and "halffilled" CuOr planes are too small, i.e., the "structural coherence length" (Jorgensen et al. 1991) is smaller than superconductivity coherence length ($\xi_{ab} \approx 15$ Å). It is known, for example, from ultrahigh resolution electron microscopy experiments (Horiuchi 1992), that in a YBCO sample with x=0.4 corresponding to the edge of the 60K plateau, the oxygen tends to become ordered in clusters of very small size (from 8 to 30 Å). However, another explanation is possible, too: even if the oxygen ordering regions are big enough, full identity of CuO_r layers, i.e., their mirror symmetry with respect to the R ion plane, is necessary for high- T_c superconductivity to appear. If this idea is valid, a half of OII–OII "sandwiches" containing K_2 centers of the K_{10}^{10} -type (see fig. 48a) has to be superconducting, and another half with K_2 centers of the K_{10}^{01} -type, non-superconducting, as shown in fig. 50. The superconducting volume fraction can be determined then by relative intensities of the K_4 - and K_2 -resonance lines as follows (Bakharev et al. 1994):

$$V_{\rm sc} = I(K_4) + \frac{1}{2}I(K_2). \tag{300}$$

The open symbols in fig. 45b show the results of the most detailed measurement of the Meissner effect in YBa₂Cu₃O_{6+x} (Graf et al. 1990), and the asterisks correspond to the sum of the Gd³⁺ EPR line intensities (eq. 300) for the same compounds (Pekker et al. 1991, Rockenbauer et al. 1992). As one can see, in the range of the 60 K plateau (0.5 < x < 0.8), the data obtained by different methods are in excellent agreement.

6.2. Inhomogeneous and homogeneous broadening of the energy levels

The above picture of five possible kinds of the crystal field potentials (K_0-K_4) formed by ideally ordered CuO_x layers of OI and/or OII types is definitely oversimplified. In reality, the oxygen distribution in the CuO_x layers is not homogeneous, so that the crystal field potential varies from one R ion to another. For example, the Tm NMR studies of the TmBa₂Cu₃O₆ sample at 4.2 K have shown the inhomogeneous halfwidth at a half maximum δ for the Tm resonance line in a field $H_0 \perp c$ to vary with frequency ν according to the following expression (Egorov et al. 1992):

$$\delta^2 = \delta_0^2 + \delta_1^2 v^2, \tag{301}$$

where $\delta_0 = 330 \text{ Oe}$ and $\delta_1 = 6 \text{ Oe}/\text{MHz}$. Thus, thulium nuclei feel the internal magnetic fields δ_0 of about 300 Oe, independent of the external conditions. The only possible source of such strong fields in the antiferromagnet TmBa₂Cu₃O₆ are Cu²⁺(2) ions. Since the Tm³⁺ ion occupies a centrosymmetric site, no fields can appear in an ideal crystal lattice. Therefore, the internal field can be attributed only to local distortions of the lattice symmetry. For comparison, one may note that in Y_{0.97}Yb_{0.03}Ba₂Cu₃O₆ the internal fields at the sites of Yb³⁺ impurity ions are as large as 1600 Oe (Hodges et al. 1991a). The second term in eq. (301) can be the result of the scattering of the γ_{\perp} -parameter due to local variations of the df-electron energy levels. Since the "enhanced" γ_{\perp} -value is much greater than the ¹⁶⁹Tm nuclear gyromagnetic ratio $\gamma_I = -2\pi 354 \text{ s}^{-1} \text{ Oe}^{-1}$, the parameter δ_1 of the Gaussian NMR line can be written as follows (cf. Aminov and Teplov 1985, 1990):

$$\delta_1 \approx \sqrt{2\ln 2} \frac{2\pi}{\gamma_\perp} \frac{\Gamma}{\Delta},\tag{302}$$

where Γ is the halfwidth of the $\Gamma_4^{(1)} - \Gamma_5^{(1)}$ transition (see table 5). Therefore, it follows from eq. (302) that the halfwidth Γ is of about 3.4 cm⁻¹ which is in a good agreement

Table	33
14010	22

Pre-exponential factors $R_{1,2}$ in the thulium nuclear relaxation rates, correlation times τ_c of the hyperfine field fluctuations, homogeneous ($\Gamma_0 = \hbar/\tau_c$) and inhomogeneous (Γ) half-widths of the Tm³⁺ ion transitions from the ground singlet to the nearest doublet state ($\Gamma_4 - \Gamma_5$) at the tetragonal sites in TmBa₂Cu₃O_{5+r} crystals (x = 0 - 0.4)^a

x	v (MHz)	T (K)	Γ (cm ⁻¹)	Relaxation rate	$R_{1,2}$ (10 ⁶ s ⁻¹)	$\tau_{\rm c} \ (10^{-11} \ {\rm s})$	Γ ₀ (cm ⁻¹)
0.0	49.5	18–30	3.4	T_{1}^{-1}	1.1	0.32	1.7
				T_{2}^{-1}	1.9	0.32	1.7
0.2	68	30-40	7.4	T_{1}^{-1}	0.9	0.58	0.92
				T_{2}^{-1}	5.1	0.58	0.92
0.4	68	30-35	12.5	T_{1}^{-1}	1.8	0.82	0.65
				T_{2}^{-1}	7.4	0.82	0.65
$(T_{\rm C} = 23 {\rm K})$	48	25–40	-	T_{2}^{-1}	3.5	0.72	0.74

^a Data from Egorov et al. (1992) and Dooglav et al. (1992).

with the value of 3.2 cm^{-1} for the magnetically diluted system Tm:YBa₂Cu₃O_{6.1} at low temperatures (Osborn and Goremychkin 1991). With the oxygen content increasing from 6.0 to 6.4, the tetragonal symmetry of the crystal field generally survives, but the crystal structure disorder increases. Measuring the broadening of the low field wing of the Tm NMR spectrum in a field $H_0 \perp c$, one can estimate (Egorov et al. 1992) the inhomogeneous width of the Tm³⁺ energy levels vs. oxygen content (see fourth column of table 33). Apparently, such large Γ -values should be explained as random splitting of the excited doublet $\Gamma_5^{(1)}$ by the crystal fields of low symmetry in a distorted lattice. However, one should note that these distortions are already partly ordered in the sample with x = 0.4, decreasing further at larger oxygen contents. The static displacements of O(1) atoms, perpendicular to the CuO chains by ~0.07 Å, existing even in a nearly stoichiometric compound with x = 0.98 (Schweiss et al. 1994), may well be accounted for by the inhomogeneous half-width $\Gamma = 1.4 \text{ cm}^{-1}$ observed in the sample Tm:YBa₂Cu₃O_{6.9} at low temperatures (Osborn and Goremychkin 1991).

The homogeneous half-width of the Tm^{3+} energy levels can be deduced from the thulium nuclear relaxation rates at elevated temperatures. Let the crystal field be of the tetragonal symmetry. Then, in the external magnetic field H_0 perpendicular to the *c*-axis, the doublet $\Gamma_5^{(1)}$ (at the energy Δ) is not split, and nuclear relaxation rates due to the fast fluctuations of the hyperfine magnetic fields are given by the following expressions (cf. eqs. 186, 187):

$$T_1^{-1} = \left[2 \left(\frac{A_{\rm J}}{\hbar} \right)^2 a^2 + \frac{1}{2} (\omega_0 - \omega_I)^2 \right] \tau_{\rm c} \exp\left(\frac{-\Delta}{k_{\rm B}T} \right) = R_1 \exp\left(\frac{-\Delta}{k_{\rm B}T} \right), \tag{303}$$

$$T_2^{-1} = \frac{1}{2}T_1^{-1} + 5(\omega_0 - \omega_I)^2 \tau_c \exp\left(\frac{-\Delta}{k_B T}\right) = R_2 \exp\left(\frac{-\Delta}{k_B T}\right),$$
(304)

where A_J is the free-ion hyperfine interaction constant; $a = \langle \Gamma_5^{(1)} | J_z | \Gamma_5^{(1)} \rangle$ is the matrix element; $\omega_0 - \omega_I = (\gamma_\perp - \gamma_I) H_0$ is the difference in frequencies between enhanced and ordinary NMR; and τ_c is the life-time of the 4f-electron shell in the excited state $|\Gamma_5^{(1)}\rangle$. Having the correlation time

$$\tau_{\rm c} = \frac{2R_2 - R_1}{10(\omega_0 - \omega_I)^2},\tag{305}$$

as follows from eqs. (303) and (304), one can estimate the half-width of the homogeneously broadened Tm³⁺ level: $\Gamma_0 \approx \hbar/\tau_c$. The experimental results on the Tm nuclear relaxation at elevated temperatures (Egorov et al. 1992, Dooglav et al. 1992), summarized in table 33, clearly show the homogeneous half-width of the $\Gamma_5^{(1)}$ energy level to decrease sharply from 1.7 cm⁻¹ down to 0.65 cm⁻¹ with oxygen doping from x=0 to x=0.4. It means that τ_c is defined by the transfer of the electron excitation to the neighbouring Tm³⁺ ions due to magnetic dipolar (or other) interactions of the $(J_{i+}J_{k-}+J_{i-}J_{k+})$ type, so that

$$\frac{1}{\tau_{\rm c}} \sim \sum_{j} (r_j^2 - 3z_j^2)^2 r_j^{-10} g(\Delta \omega).$$
(306)

Let us choose for definiteness the g-function in a Lorentzian form (172), with $\Delta \omega =$ $(\Delta_1 - \Delta_i)/\hbar$ being the difference (in frequency units) between the excited $\Gamma_5^{(1)}$ -state energies of the first and *j*-th Tm³⁺ ions. Then the experimental data on Γ_0 (last column in table 33) can be explained, if one takes the energy difference $(\Delta_1 - \Delta_i) = 1.5 - 2 \text{ cm}^{-1}$ for the nearest neighbouring Tm sites, which corresponds to approximately 1% variations of the Tm^{3+} energy splitting from site to site. This energy detuning transforms into Tm NMR frequency detuning which, in its turn, results in a frozen spin diffusion of thulium nuclei. The consequences of the hampered nuclear spin diffusion in Tm 1-2-3 materials will be considered in the next subsection. Here we have to emphasize that the effect of the Tm NMR frequency detuning does not disappear in the absence of an external field. Even for the most perfect crystal structure (x=0) compounds, the Tm NMR line half-width extrapolated to zero NMR frequency exceeds 300 Oe, and in samples with x > 0 the local field can be an order of magnitude higher (Hodges et al. 1991a,b) (for example, see the low-field wing of the Tm spectrum in fig. 49a). The existence of such strong inhomogeneous Tm NMR lines broadening due to $Cu^{2+}(2)$ local fields, makes it unnecessary to take into account the inhomogeneity of internal fields (~20 Oe) caused by the vortex lattice in the superconducting samples (Brom and Alloul 1991, Carretta and Corti 1992).

6.3. Effect of copper-oxygen paramagnetic complexes on nuclear magnetic relaxation

In order to analyze the magnetic properties of oxygen-deficient 1-2-3 compounds containing different kinds of copper-oxygen chain fragments (fig. 46), we shall use a

simple description relating the formal copper valence to the local oxygen occupancy (Schleger et al. 1994). It is supposed that a copper neighboured by oxygen vacancies only (chain of length L=0) is formally monovalent. An isolated oxygen (chain of length L=1) will oxidize the two neighbouring coppers, creating two $Cu^{2+}(1)$ paramagnetic ions. At low oxygen concentration, where the oxygen occupancy is randomly distributed, this predicts a (1-2x) dependence of the $Cu^+(1)$ count, as observed experimentally (Tolentino et al. 1992). A chain of length L=2 will require placement of four electron holes. Three holes may be placed on the copper, giving three $Cu^{2+}(1)$ ions, but the fourth hole has mainly O 2p character. This O 2p hole, unlike the Cu 3d hole, is not bound to one particular oxygen site, but may hop. Thus, the process of oxygen addition results in the formation of unpaired electron spins, and the oxygen atoms entering into the crystal lattice are expected to give rise to a rich variety of the static and dynamic internal electric and magnetic fields. Let us see how these fields can influence the Tm nuclear relaxation at temperatures below 4.2 K.

The T_1 and T_2 relaxation times in different aligned powdered samples TmBa₂Cu₃O_{6+x} aged at room temperature for more than one year were measured at frequencies v from 42 to 50 MHz, but when measuring in the field $H_0 \perp c$, the H_0 value was always chosen according to the $H_0/v = 2\pi/\gamma_a = 0.189$ kOe/MHz condition (Bakharev et al. 1994). In this case only powder particles with the *a* axes lying close to H_0 direction were influenced by the resonant $H_1 \approx 100$ Oe radio-frequency magnetic field. The relaxation times T_2 of the Tm transverse magnetization were measured by the Hahn method $(\pi/2-\tau-\pi-echo A_{2\tau})$. The results of measurements at T = 1.5 K in the field $H_0 \parallel a$ were fitted well by the following expression:

$$A_{2\tau} = A_{\rm G} \exp\left[-\frac{1}{2} \left(\frac{2\tau}{T_{2\rm G}}\right)^2\right] + A_{\rm L} \exp\left(-\frac{2\tau}{T_{2\rm L}}\right). \tag{307}$$

It is known that the spin echo decay is influenced not only by the spin-spin relaxation, i.e., "flip-flop" processes, but also by "spectral diffusion" and "instantaneous diffusion" processes (Klauder and Anderson 1962). If the NMR line is inhomogeneously broadened so much that only a small part of a total amount of spins can be excited by radiofrequency pulses, all these processes become as slow as in the case of a magnetically diluted system. The experimental data (Bakharev et al. 1994) allowed one to conclude that thulium T_2 times in TmBa₂Cu₃O_{6+x} compounds are strongly influenced by the inhomogeneous broadening (of both electric and magnetic origin) which definitely increases in higher external magnetic fields. However, the large difference in T_{2G} - and T_{2L} -values (T_{2G} = 65 µs for all three phases T, OII and OI; whereas T_{2L} changes from 75 μ s for T-phase through 100 μ s for OII-phase to more than 400 μ s for OI-phase) as well as the clearly pronounced maximum in the $T_{2G}(H)$ dependence, corresponding to $\gamma\text{-values}$ between γ_a and γ_b (the feature expected for a "powder spectrum" of a good crystalline material) made it possible to distinguish between two types of Tm³⁺ centers that can be naturally attributed to two different fractions of the samples, i.e., slightly disordered (A_G) and heavily disordered ones (A_L) . Furthermore, the obvious correlation

between $A_{\rm G}$ and the superconducting volume fraction in TmBCO samples allowed one to attribute the slightly disordered fraction to the superconducting volume. The common behaviour of the nuclear spin-lattice relaxation for all ¹⁶⁹Tm³⁺ centers has definitely given evidence that both fractions (represented by $A_{\rm G}$ and $A_{\rm L}$) are closely mixed together in a finely dispersed form.

The thulium nuclear spin-lattice relaxation times T_1 in TmBa₂Cu₃O_{6+x} were measured using $\pi/2-\pi-t-\pi/2-\pi$ pulse sequence and observing the recovery of the spin echo intensity A_t (Bakharev et al. 1993, 1994). It appeared that for all samples at $T \leq 4.2$ K, the recovery curve was fairly well described by "Förster's law":

$$1 - \frac{A_t}{A_\infty} = \exp\left(-\sqrt{\frac{t}{T_1}}\right). \tag{308}$$

It is known (Blumberg 1960, Tse and Hartmann 1968, McHenry et al. 1972) that the kinetics (308) is typical for disordered systems in which a strong inhomogeneous NMR line broadening takes place and nuclear spin diffusion is hampered due to the Larmor frequencies differences of the nuclear spins located in the neighbouring crystal lattice sites. In such systems the nuclear spins at low temperatures relax directly via paramagnetic centers, well coupled with phonons. When paramagnetic centers with $S = \frac{1}{2}$ are randomly distributed in a crystal lattice, the nuclear spin-lattice relaxation rate is determined as follows:

$$\frac{1}{T_1} = \frac{4}{9}\pi^3 \mu_{\rm B}^2 N_0^2 \gamma_{\perp}^2 g_{\parallel}^2 \frac{\tau_{\rm c}}{1 + \omega^2 \tau_{\rm c}^2} \left(1 - \tanh^2 \frac{g_{\parallel} \mu_{\rm B} H_0}{2k_{\rm B} T} \right),\tag{309}$$

where N_0 is the concentration of paramagnetic centers; $\omega = \gamma H$ is the NMR frequency; $\tau_{\rm c}$ is a correlation time for local field fluctuations created by paramagnetic centers at nuclei's sites. The eq. (309) is valid in the case of purely dipolar I-S interaction, the g_{\parallel} and γ_{\perp} -values should be interpreted as g- and γ -tensor components, corresponding to the directions along and transverse to the spin quantization axis, i.e., the external field H_0 . The T_1 -measurements at frequencies of 45–50 MHz and temperatures from 4.2 down to 0.04 K have made it possible to conclude (Bakharev et al. 1993, 1994, Teplov et al. 1995): (i) the correlation time $\tau_c(\sim 10^{-8} \text{ s})$ does not depend much on oxygen content (x = 0, ..., 1)and temperature; (ii) the mean length L of the CuO chain fragments equals 2 at x=0.4and starts to grow sharply at x > 0.4 reaching L = 22 at x = 1.0; (iii) the concentration N_0 of paramagnetic centers is proportional to the concentration of pairs of "terminating" $Cu^{2+}(1)$ jons in CuO chains, increasing roughly as x^2 at x=0-0.4 and then decreasing drastically down to 0.0042 per unit cell at x = 1.0 (the specific heat measurements have given $n_2 = 0.0044$ per unit cell for x = 1.0 (Lee et al. 1991). The most interesting fact is that the concentration N_0 of paramagnetic centers at the T–O transition (see fig. 51) reaches the maximum value of 0.07 per unit cell which exactly coincides with the critical hole density for both the metallic conduction and superconductivity $(4 \times 10^{20} \text{ cm}^{-3})$, Tanabe et al. 1994). Having in mind that CuO chain fragments with the mean length



Fig. 51. Concentration N_0 (open circles) of paramagnetic acceptor centers in TmBa₂Cu₃O_{6+x} (Bakharev et al. 1994) and the concentration n_p (Tanabe et al. 1994) of holes in the CuO₂ planes in YBa₂Cu₃O_{6+x} vs. the oxygen content (for details see text).

L=2, corresponding to the T–O transition ($x \approx 0.4$), contain one hole per each fragment, one arrives at the following assumption: paramagnetic centers (complexes) causing the nuclear spin-lattice relaxation in TmBa₂Cu₃O_{6+x} compounds at temperatures $T \ll T_c$ can be formed or induced by the "two-links" Cu–O–Cu–O–Cu chain fragments.

The kinetics of the exp $(-\sqrt{t/T_1})$ type is characteristic for three-dimensional disordered systems. The particular feature of 1-2-3 compounds (i.e., their layered structure) starts to exhibit itself in the $\exp(-\sqrt[3]{t/T_1})$ -type nuclear spin relaxation kinetics, when the concentration of paramagnetic centers is very high, so that the mean distance between them becomes comparable with the plane separation distance, i.e., the lattice parameter c (Krjukov et al. 1994, Bakharev et al. 1995a). The "1/3" power is known to be valid for the case of the 2D-distribution of the acceptors (Klafter and Blumen 1984). The concentration of paramagnetic centers is particularly high if the oxygen content is close to 0.4 and the sample is prepared by quenching in liquid nitrogen from 750°C (i.e., from a tetragonal region of the phase diagram). If such a sample is allowed to "age" after quenching (Veal et al. 1990, Jorgensen et al. 1990a), the oxygen diffusion proceeds due to $O(5) \rightarrow O(1)$ jumps which results in an increase of the mean chain length and a decrease of the amount of "two-links" fragments, carrying paramagnetic centers-acceptors. Consequently, the relaxation time of the Tm nuclei in such a sample measured at liquid helium temperatures is expected to grow with the increase of the room-temperature annealing time t_{RTA} . The $T_1(t_{RTA})$ dependence for such a quenched sample with $x \approx 0.4$ is shown in fig. 52a; the magnetization recovery at T = 1.5 K ($H_0 || a$) was found to obey the $\exp(-\sqrt[3]{t/T_1})$ -law in the whole range of t_{RTA} up to two weeks. Comparing the $T_1(t_{RTA})$ -curve with the $T_c(t_{RTA})$ -curve (fig. 52b), one realizes that the most drastic changes in T_1 -values (i.e., in the concentration of paramagnetic centers, too) appear at small t_{RTA} 's, when only one jump $O(5) \rightarrow O(1)$ may really occur with no noticeable signs of the $T \rightarrow O$ transition at this early stage of the oxygen ordering



Fig. 52. Spin-lattice relaxation time T_1 of ¹⁶⁹Tm nuclei measured at 1.5 K in the field $H_0 = 2\pi v/\gamma_a = 9.1$ kOe (a), and the critical temperature T_c onset (b) of the N₂-quenched TmBa₂Cu₃O_{6.4} powder allowed to "age" at room temperature for the time t_{RTA} (Krjukov et al. 1994).

process. The characteristic time τ_{RTA} of ~1 hour seen in fig. 52a is similar with that measured in resonant Raman scattering experiments (Hadjiev et al. 1993), which means that the oxygen 2D-diffusion coefficient at room temperatures is equal to ~10⁻¹⁹ cm²/s, in excellent agreement with the results of direct measurements (Mogilevsky et al. 1994).

The Tm relaxation in the TmBa₂Cu₃O_{6.5} sample has been found to change the 2Dbehaviour ("1/3"-power) to the 3D-behaviour ("1/2"-power) at temperatures decreasing below 1 K (Bakharev et al. 1995a). Since the paramagnetic centers are located at the boundaries of superconducting microdomains (Bakharev et al. 1993, 1994), one can assume the average distance r between paramagnetic centers to be of the order of the mean length L of CuO chain fragments. In the equilibrium x=0.5 sample, the value of L has been found to be approximately 6a or 2c, thus, the critical value of $r_c \approx L$, separating 2D- and 3D-regimes of the relaxation kinetics from one another, indeed appears to be close to the lattice parameter c. Thus, the concentration of paramagnetic acceptor centers seems to decrease at low temperatures. Such an effect of thermal depopulation cannot take place in a simple two level system with $S = \frac{1}{2}$. However, it is consistent with a model of a singlet-doublet (or singlet-triplet) system. Indeed, the effect of thermal depopulation must occur in a system where the paramagnetic centers (or copper-oxygen complexes) in the CuO₂ planes have a nonmagnetic (singlet) ground state, separated from an excited magnetic state by an energy gap of the order of 1 K (Bakharev et al. 1995a, Teplov et al. 1995). A similar assumption has been discussed earlier (Schreiner et al. 1992, Baak et al. 1993) in connection with an excess contribution to the specific heat of YBCO compounds at low temperatures.

Measurements at LBL (Berkeley) of the specific heat C of $YBa_2Cu_3O_7$ in magnetic fields showed the presence of both a Schottky anomaly and the coefficient of the "linear term" in C (Phillips et al. 1992a). In the model proposed to explain these results, the Schottky anomaly arises from a low concentration (n_2) of Cu²⁺ magnetic moments that are also responsible for the zero-field "up-turn" in C/T. The importance of n_2 is related to its negative correlation with certain superconducting-state properties. These correlations were based on measurements on a number of large polycrystalline samples prepared in seven different research groups. They show that the strong sample-to-sample variation in parameters derived from specific-heat data are associated with corresponding variations in the volume fraction of superconductivity f_s . The Cu²⁺ moments are associated with the non-superconducting material, and n_2 is proportional to its amount (Phillips et al. 1989, 1990, 1992b, 1994). It is shown in fig. 53 by open circles that the superconducting volume fraction f_s as derived from the specific heat measurements, reduces according to approximate relation $f_s = 1 - n_2/0.012$, where n_2 is given in (mole Cu²⁺/mole YBCO). Solid circles and asterisks in fig. 53 represent $V_{\rm SC}$ vs. N_0 , and $A_{\rm G}/(A_{\rm G} + A_{\rm L})$ vs. N_0 dependencies, respectively, as combined on the basis of T_1 -, T_2 -, and diamagnetic susceptibility data (Bakharev et al. 1994) for the series of TmBa₂Cu₃O_{6+x} samples. The excellent agreement of different results shown in fig. 53 makes it possible to conclude that $N_0 = n_2$, i.e., one type of paramagnetic centers (complexes) seems to be observed in both specific-heat and Tm NMR-experiments at low temperatures. Keeping in mind the above conclusion about "two-link" chain fragments at x = 0.4 (see fig. 51), one can further assume those fragments to be accounted for by the observed effects in specific heat and NMR measurements of $x \approx 1$ samples, as well. The estimation of the concentration of "two-links" fragments $x^2(1-x)^2/6$ in the sample of optimum oxygen content (x=0.94, $T_{\rm C} = \max$, Graf et al. 1990), yields 5×10^{-4} per unit cell, which is close to the value of 2.5×10^{-4} per unit cell, deduced by Emerson et al. (1994) from the specific heat data for well oxygenated samples (Sanchez et al. 1992).

Thus, the most important result obtained in both Tm NMR and specific heat measurements is that magnetic properties of oxygen-deficient RBa₂Cu₃O_{6+x} compounds at low temperatures are determined by *intrinsic* paramagnetic centers. What could be the structure of these paramagnetic centers or copper–oxygen complexes? As was already mentioned above, the O 2p hole is not bound to one particular oxygen site in an isolated CuO chain fragment, but may hop. There are several possibilities for the hole to produce copper–oxygen paramagnetic complexes. (i) The hole may hop over four oxygen atoms [two O(1) and two O(4)] around the central Cu²⁺(1) ion in the "two-links" chain fragment resulting in the appearance of a ferromagnetically coupled pair of terminating Cu²⁺(1) ions. (ii) The hole may hop up or down to the CuO₂ planes forming a pentanuclear copper cluster with a total spin S=2 and/or a tetranuclear copper cluster with $S=\frac{3}{2}$ (Eremin and Sigmund 1994, Bakharev et al. 1995b). (iii) The hole may be placed on the nearest neighbouring Cu(2) site resulting in an appearance of a spin hole at this site and, consequently, a small ferromagnetic polaron (Wachter et al. 1994).

Therefore, one can expect a rich variety of paramagnetic copper-oxygen complexes to appear in oxygen-deficient $RBa_2Cu_3O_{6+x}$ compounds. Whatever the real structure and



Fig. 53. Superconducting volume fraction f_s of YBa₂Cu₃O_{6+x} as derived from the specific heat data (open circles) vs. the concentration n_2 of the magnetic Cu²⁺ ions (Phillips et al. 1994); the diamagnetic susceptibility $-4\pi\chi$ of TmBa₂Cu₃O_{6+x} at liquid helium temperature (solid circles) vs. the concentration N_0 of paramagnetic acceptor centers, the latter derived from measurements of the Tm nuclear spin-lattice relaxation; the relative amount $A_G/(A_G + A_L)$ of "ordered" Tm-sites (*, see eq. 307) vs. the concentration N_0 of the paramagnetic centers (Bakharev et al. 1994).

properties of the paramagnetic complexes are, one has to take their presence into account when analysing the relaxation behaviour of all sorts of nuclear spins in this system at temperatures below T_c .

7. Conclusion

Concluding this chapter we will emphasize once more some distinctive features of dielectric lanthanide magnets, which have not attracted appropriate attention as yet.

- Internal magnetic fields in these compounds are highly inhomogeneous; the probe magnetic moments are quantized differently at different positions within a crystal lattice, thus their response to applied steady and alternating fields is rather complicated.
- (2) The magnetic properties of lanthanide compounds are highly sensitive to impurities. The crystal structure distortions are accompanied by rearrangement of the lower energy levels of host lanthanide ions. This rearrangement is essential for ions close to an impurity and cannot be considered as small perturbations in crystals with dense packing of lanthanide ions.

These and other specific properties of lanthanide compounds are associated with the strong localization of paramagnetic 4f electrons, and they can be calculated within the framework of modern crystal field theories. We have shown that a simple exchange charge model allows one to interpret consistently a wide scope of diverse experimental results. With a single set of model parameters it appeared possible to explain the spectra, induced magnetostriction, magneto-acoustic phenomena, electric field effects in different lithium–lanthanide double fluorides. For regular and mixed crystals with zircon structure the model calculations have allowed prediction of the parameters of interionic interactions,

determining the structural phase transitions in these compounds. Detailed analysis of the crystal field structure in the RF₃ crystals made it possible to predict the directions of the magnetic moments in different quasi-doublet states of the non-Kramers ions.

We could not consider all magnetic properties in full detail. This concerns especially problems of excitation spectra of the lanthanide crystals in the magnetically ordered states and in an applied magnetic field, migration of excitations, the influence of magnetic fields on thermal conductivity, magneto-optical phenomena, and relaxation in the critical region. However, we hope that this review reflects properly the modern situation in the magnetism of the nonmetallic lanthanide compounds and that the comprehensive information presented will be useful as a reference.

Acknowledgements

One of the authors (BZM) is grateful to the Royal Society for a Kapitza Fellowship and to Prof. B. Bleaney and Dr. J.M. Baker for hospitality at the Clarendon Laboratory, Oxford University.

References

- Abbas, Y., J. Rossat-Mignod, G. Quezel and C. Vettier, 1974, Solid State Commun. 14, 1115.
- Abbas, Y., J. Rossat-Mignod, F. Tcheou and G. Quezel, 1977, Physica B 86–88, 115.
- Abdulsabirov, R.Yu., I.S. Konov, S.L. Korableva, S.N. Lukin, M.S. Tagirov and M.A. Teplov, 1979, Zh. Eksp. Teor. Fiz. 76, 1023.
- Abdulsabirov, R.Yu., Z.A. Kazei, S.L. Korableva and D.N. Terpilovskii, 1993, Fiz. Tverd. Tela 35, 1876.
- Abdulsabirov, R.Yu., A.V. Vinokurov, S.L. Korableva, B.Z. Malkin and A.L. Stolov, 1995, in: Xth Feofilov symposium on spectroscopy of crystals activated by rare earth and transitional ions, Abstracts, St. Petersburg, 1995, p. 331.
- Abragam, A., 1961, The Principles of Nuclear Magnetism (Clarendon Press, Oxford).
- Abragam, A., and B. Bleaney, 1970, Electron Paramagnetic Resonance of Transition Ions (Clarendon Press, Oxford).
- Abragam, A., and B. Bleaney, 1982, Proc. R. Soc. London Ser. A 382, 61.
- Abragam, A., and B. Bleaney, 1983, Proc. R. Soc. London Ser. A 387, 221.
- Abragam, A., and M. Goldman, 1982, Nuclear Magnetism: Order and Disorder (Clarendon Press, Oxford).

- Abraham, M.M., J.M. Baker, B. Bleaney, A.A. Jenkins, P.M. Martineau and J.Z. Pfeffer, 1991, Proc. R. Soc. London Ser. A 435, 605.
- Abraham, M.M., J.M. Baker, B. Bleaney, J.Z. Pfeffer and M.R. Wells, 1992, J. Phys.: Condens. Matter 4, 5443.
- Aharony, A., and B.I. Halperin, 1975, Phys. Rev. Lett. **35**, 1308.
- Aharony, A., and P.C. Hohenberg, 1976, Phys. Rev. B 13, 3081.
- Ahlers, G., A. Kornblit and H.J. Guggenheim, 1975, Phys. Rev. Lett. 34, 1227.
- Aldred, A.T., 1984, Acta Crystallogr. Sect. B 40, 569.
- Aleksandrov, I.V., B.V. Lidskii, L.G. Mamsurova, M.G. Neigaus, K.S. Pigalskii, K.K. Pukhov, N.G. Trusevitch and L.G. Tcherbakova, 1985, Zh. Eksp. Teor. Fiz. 89, 2230.
- Aleonard, S., and C. Pouzet, 1968, J. Appl. Crystallogr. 1, 113.
- Aligia, A.A., A.G. Rojo and B.R. Alascio, 1988, Phys. Rev. B **38**, 6604.
- Allenspach, P., A. Furrer and F. Hulling, 1989, Phys. Rev. B 39, 2226.
- Allenspach, P., U. Staub, J. Faut, M. Guillaume, A. Furrer and H. Mutka, 1991, in: Neutron-Streuung

(Progress Report) Januar-Dezember 1990, LNS-154, pp. 22-23.

- Allenspach, P., B.W. Lee, D. Gajewski, M.B. Maple, S.I. Yoo and M.J. Kramer, 1993, J. Appl. Phys. 73, 6317.
- Allsop, A.L., B. Bleaney, G.J. Bowden, N. Nambudripad, N.J. Stone and H. Suzuki, 1981, Hyperfine Int. 10, 849.
- Als-Nielsen, J., 1976, Phys. Rev. Lett. 37, 1161.
- Als-Nielsen, J., L.M. Holmes, F.K. Larsen and H.J. Guggenheim, 1975, Phys. Rev. B 12, 191.
- Al'tshuler, S.A., 1966, Zh. Eksp. Teor. Fiz. Pis'ma Red. 3, 177.
- Al'tshuler, S.A., and B.M. Kozyrev, 1972, Elektronnii Paramagnitnii Rezonans Soyedinenii Elementov Promezhutochnikh Grupp (Nauka, Moscow).
- Al'tshuler, S.A., and M.A. Teplov, 1967, Zh. Eksp. Teor. Fiz. Pis'ma Red. 5, 209.
- Al'tshuler, S.A., and M.A. Teplov, 1978, Problemy Magnitnogo Rezonansa (Nauka, Moscow) p. 14.
- Al'tshuler, S.A., F.L. Aukhadeev and M.A. Teplov, 1969, Zh. Eksp. Teor. Fiz. Pis'ma Red. 9, 46.
- Al'tshuler, S.A., F.L. Aukhadeev, V.A. Grevtsev and M.A. Teplov, 1975, Zh. Eksp. Teor. Fiz. Pis'ma Red. 22, 159.
- Al'tshuler, S.A., A.V. Duglav, A.Kh. Khasanov, I.G. Bol'shakov and M.A. Teplov, 1979, Zh. Eksp. Teor. Fiz. Pis'ma Red. 29, 680.
- Al'tshuler, S.A., V.I. Krotov and B.Z. Malkin, 1980, Zh. Eksp. Teor. Fiz. Pis'ma Red. 32, 232.
- Al'tshuler, S.A., A.A. Kudryashov, M.A. Teplov and D.N. Terpilovskii, 1982, Zh. Eksp. Teor. Fiz. Pis'ma Red. 35, 239.
- Al'tshuler, S.A., R.Yu. Abdulsabirov, F.L. Aukhadeev, L.A. Burnagina, A.G. Volodin, R.Sh. Zhdanov, S.L. Korableva, V.I. Krotov, B.Z. Malkin, I.P. Petrova, M.S. Tagirov, M.A. Teplov and D.N. Terpilovskii, 1984, Paramagnitnii Rezonans, No. 20 (Publ. University Kazan) p 29.
- Al'tshuler, S.A., B.Z. Malkin, M.A. Teplov and D.N. Terpilovskii, 1985, in: Soviet Scientific Reviews, Section A, Physics Reviews, Vol. 6, ed. I.M. Khalatnikov (Harwood Academic Publishers) pp. 61-159.
- Aminov, L.K., 1978, Spektroskopiya Kristallov (Nauka, Leningrad) p. 116.
- Aminov, L.K., 1981, Fiz. Tverd. Tela 23, 2167.
- Aminov, L.K., and B.I. Kochelaev, 1962, Zh. Eksp. Teor. Fiz. 42, 1303.
- Aminov, L.K., and Yu.Yu. Kostetskii, 1990, Phys. Status Solidi (b) **158**, 595.

- Aminov, L.K., and M.A. Teplov, 1985, Usp. Fiz. Nauk. 142, 49 [Sov. Phys.-Usp. 28, 762].
- Aminov, L.K., and M.A. Teplov, 1990, in: Soviet Scientific Reviews, Section A, Physics Reviews. Vol. 14, ed. I.M. Khalatnikov (Harwood Academic Publishers) p. 1.
- Aminov, L.K., M.S. Tagirov and M.A. Teplov, 1980, Zh. Eksp. Teor. Fiz. 79, 1322.
- Aminov, L.K., M.S. Tagirov and M.A. Teplov, 1982, Zh. Eksp. Teor. Fiz. 82, 224.
- Aminov, L.K., A.A. Kudryashov and M.A. Teplov, 1983, Paramagnitnii Rezonans, No. 19 (Publ. University Kazan) p. 64.
- Aminov, L.K., A.A. Kudryashov, M.S. Tagirov and M.A. Teplov, 1984, Zh. Eksp. Teor. Fiz. 86, 1791.
- Aminov, L.K., A.G. Volodin, M.S. Tagirov and M.A. Teplov, 1985, in: Proc. 2nd Conf. on Modern Methods in Radiospectroscopy, Reinhardsbrunn, DDR, part 2, p. 40.
- Aminov, L.K., T.B. Bogatova, I.N. Kurkin, I.Kh. Salikhov, S.I. Sakhaeva and M.A. Teplov, 1986, Zh. Eksp. Teor. Fiz. 91, 262.
- Aminov, L.K., A.G. Volodin, T.V. Kropotova, V.V. Naletov, A.R. Safiullin, M.S. Tagirov and M.A. Teplov, 1988, Paramagnitnii Rezonans, No. 22 (Publ. University Kazan) p. 131.
- Aminov, L.K., A.V. Vinokurov, I.N. Kurkin, Yu.Yu. Kostetskii, S.L. Korableva, I.Kh. Salikhov, S.I. Sakhaeva and M.A. Teplov, 1989, Phys. Status Solidi (b) 152, 191.
- Aminov, L.K., I.N. Kurkin, I.Kh. Salikhov and S.I. Sakhaeva, 1990a, Fiz. Tverd. Tela 32, 2705.
- Aminov, L.K., B.Z. Malkin, M.A. Koreiba, S.I. Sakhaeva and V.R. Pekurovskii, 1990b, Opt. & Spektrosk. 68, 835.
- Aminov, L.K., M.S. Tagirov, M.A. Teplov and A.G. Volodin, 1990c, Hyperfine Int. 59, 255.
- Anders, A.G., and S.V. Volotskii, 1992, Supercond. Phys. Chem. Techn. 5, 575.
- Anders, A.G., S.V. Volotskii, S.V. Startsev, A. Feger and A. Orendaneva, 1995, Fiz. Nizk. Temp. (Kiev) 21, 52.
- Anderson, R.J., J.M. Baker and R.J. Birgeneau, 1971, J. Phys. C 4, 1618.
- Andres, K., 1973, Phys. Rev. B 7, 4295.
- Andres, K., 1978, Cryogenics 18, 473.
- Andres, K., and E. Bucher, 1968, Phys. Rev. Lett. 21, 1221.
- Andres, K., and E. Bucher, 1971, J. Appl. Phys. 42, 1522.

- Andres, K., and S. Darack, 1977, Physica B+C 86-88, 1071.
- Andronenko, S.I., and A.N. Bazhan, 1989, Fiz. Tverd. Tela 31, 35.
- Andronenko, S.I., V.A. Ioffe and Yu.P. Udalov, 1981, Fiz. Tverd. Tela 23, 2516.
- Andronenko, S.I., A.N. Bazhan, I.A. Bondar', V.A. Ioffe, B.Z. Malkin and L.P. Mezentsceva, 1983, Fiz. Tverd. Tela 25, 423 [Sov. Phys.-Solid State 25, 239].
- Antipin, A.A., B.N. Kazakov, S.L. Korableva, R.M. Rakhmatullin, Yu.K. Chirkin and A.A. Fedii, 1978, Izv. Vyssh. Uchebn. Zaved. Fiz. 9, 93.
- Antipin, A.A., I.S. Konov, S.L. Korableva, R.M. Rakhmatullin, M.S. Tagirov, M.A. Teplov and A.A. Fedii, 1979, Fiz. Tverd. Tela 21, 111.
- Armbruster, A., R.E. Thoma and H. Wehcle, 1974, Phys. Status Solidi (a) 24, K71.
- Atsarkin, V.A., 1980, Dinamicheskaya Polyarizatsiya Yader v Tverdykh Dielektrikakh (Nauka, Moscow).
- Aukhadeev, F.L., I.I. Valeev, I.S. Konov, V.A. Skrebnev and M.A. Teplov, 1973, Fiz. Tverd. Tela 15, 235.
- Aukhadeev, F.L., R.Sh. Zhdanov, M.A. Teplov and D.N. Terpilovskii, 1981, Fiz. Tverd. Tela 23, 2225.
- Aukhadeev, F.L., R.Sh. Zhdanov, M.A. Teplov and D.N. Terpilovskii, 1983, Paramagnitnii Rezonans, No. 19 (Publ. University Kazan) p. 3.
- Aukhadeev, F.L., V.A. Grevtsev, R.Sh. Zhdanov, B.Z. Malkin and M.A. Teplov, 1987, Paramagnitnii Rezonans, No. 21 (Publ. University Kazan) p. 77.
- Avanesov, A.G., V.V. Zhorin, B.Z. Malkin and V.F. Pisarenko, 1992, Fiz. Tverd. Tela 34, 2899.
- Avanesov, A.G., V.V. Zhorin, B.Z. Malkin and V.F. Pisarenko, 1994, Fiz. Tverd. Tela 36, 2899.
- Axe, J.D., and G. Burns, 1966, Phys. Rev. 152, 331.
- Baak, J., S.I. Mukhin, H.B. Brom, M.J.V. Menken and A.A. Menovsky, 1993, Physica C 210, 391.
- Baker, J.M., 1971, Rep. Prog. Phys. 34, 109.
- Baker, J.M., B. Bleaney, C.E. Davoust, C.A. Hutchison Jr, M.J.M. Leask, P.M. Martineau, M.G. Robinson, R.T. Weber and M.R. Wells, 1986a, Proc. R. Soc. London Ser. A 403, 199.
- Baker, J.M., C.A. Hutchison Jr and P.M. Martineau, 1986b, Proc. R. Soc. London Ser. A 403, 221.
- Baker, J.M., C.A. Hutchison Jr, M.J.M. Leask, P.M. Martineau, M.G. Robinson and M.R. Wells, 1987, Proc. R. Soc. London Ser. A 413, 515.
- Baker, J.M., B. Bleaney, M.I. Cook, P.M. Martineau, M.R. Wells and C.A. Hutchison Jr, 1988, J. Physiol. (Paris) Suppl. 49, C8-1515.

- Baker, J.M., M.I. Cook, C.A. Hutchison Jr, M.J.M. Leask, M.G. Robinson, A.L. Tronconi and M.R. Wells, 1991a, Proc. R. Soc. London Ser. A 434, 695.
- Baker, J.M., M.I. Cook, C.A. Hutchison Jr, P.M. Martineau, A.L. Tronconi and R.T. Weber, 1991b, Proc. R. Soc. London Ser. A 434, 707.
- Bakharev, O.N., A.V. Dooglav, A.V. Egorov, V.V. Naletov, M.P. Rodionova, M.S. Tagirov and M.A. Teplov, 1991, Appl. Magn. Reson. 2, 559.
- Bakharev, O.N., A.G. Volodin, A.V. Dooglav, A.V. Egorov, V.V. Naletov, M.S. Tagirov and M.A. Teplov, 1992a, in: Progress in High Temperature Superconductivity, Vol. 32, eds A.A. Aronov, A.I. Larkin and V.S. Lutovinov (World Scientific, Singapore) pp. 287–292.
- Bakharev, O.N., A.V. Dooglav, A.V. Egorov, H. Lütgemeier, M.P. Rodionova, M.A. Teplov, A.G. Volodin and D. Wagener, 1992b, Appl. Magn. Reson. 3, 613.
- Bakharev, O.N., A.G. Volodin, A.V. Dooglav, A.V. Egorov, O.V. Marvin, V.V. Naletov and M.A. Teplov, 1993, Zh. Eksp. Teor. Fiz. Pis'ma Red. 58, 630 [JETP Lett. 58, 608].
- Bakharev, O.N., A.V. Dooglav, A.V. Egorov, O.V. Marvin, V.V. Naletov, M.A. Teplov, A.G. Volodin and D. Wagener, 1994, in: Proc. 2nd Int. Workshop on Phase Separation in Cuprate Superconductors, September 4–10, 1993, Cottbus, Germany, eds E. Sigmund and K.A. Muller (Springer, Berlin) pp. 257–271.
- Bakharev, O.N., J. Witteveen, H.B. Brom, E.V. Krjukov, O.V. Marvin and M.A. Teplov, 1995a, Phys. Rev. B 51, 693.
- Bakharev, O.N., M.V. Eremin and M.A. Teplov, 1995b, Zh. Eksp. Teor. Phys. Pis'ma Red. 61, 499 [JETP Lett. 61, 515].
- Ballestracci, R., E.F. Bertaut and G. Quezel, 1968, J. Phys. & Chem. Solids 29, 1001.
- Barnes, R.G., 1979, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 2, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam) p. 387.
- Barnes, R.G., R.L. Mössbauer, E. Kankeleit and J.M. Poindexter, 1964, Phys. Rev. A 136, 175.
- Battison, J.E., A. Kasten, M.J.M. Leask and J.B. Lowry, 1975, Phys. Lett. A 55, 173.
- Beauvillain, P., C. Dupas and J.P. Renard, 1975, Phys. Lett. A 54, 436.
- Beauvillain, P., J.P. Renard and P.E. Hansen, 1977, J. Phys. C 10, L709.

- Beauvillain, P., J.P. Renard, I. Laursen and P.J. Walker, 1978a, Phys. Rev. B 18, 3360.
- Beauvillain, P., J.P. Renard, I. Laursen and P.J. Walker, 1978b, J. Phys. (Paris) Suppl. 39, C6–745.
- Beauvillain, P., C. Chappert and I. Laursen, 1980a, J. Phys. C 13, 1481.
- Beauvillain, P., J.P. Renard and J. Magarino, 1980b, J. Magn. & Magn. Mater. 15-18, 31.
- Beauvillain, P., C. Chappert, J.P. Renard, J. Seiden and I. Laursen, 1983, J. Magn. & Magn. Mater. 31–34, 1103.
- Becher, W., and H. Kalbfleisch, 1973, Phys. Status Solidi (b) 60, 557.
- Becher, W., H. Kalbfleisch and K. Melchior, 1973, Phys. Status Solidi (b) 60, K113.
- Becher, W., H. Kalbfleisch and K. Melchior, 1975, Physica B 80, 215.
- Becker, P.J., 1976, Phys. Status Solidi (b) 74, 285.
- Bednorz, J.G., and K.A. Müller, 1986, Z. Phys. B 64, 189.
- Bellesis, G.H., S. Simizu and S.A. Friedberg, 1987, J. Appl. Phys. 61, 3283.
- Belov, K.P., 1987, Magnetostriction Phenomena and their Technical Applications (Science, Moscow) p. 159.
- Belov, K.P., and V.I. Sokolov, 1977, Usp. Fiz. Nauk. 121, 285.
- Bethe, H.A., 1929, Ann. Phys. 3, 135.
- Beyers, R., B.T. Ahn, G. Gorman, V.Y. Lee, S.S.P. Parkin, M.L. Ramirez, K.P. Roche, J.E. Vazquez, T.M. Gur and R.A. Huggins, 1989, Nature 340, 619.
- Bingham, D., B. Bleaney, R.K. Day and J.B. Dunlop, 1984a, J. Phys. C 17, 1511.
- Bingham, D., M.J. Morgan and J.D. Cashion, 1984b, Proc. R. Soc. London Ser. A 391, 85.
- Birgeneau, R.J., J.K. Kjems, G. Shirane and L.G. Van Uitert, 1974, Phys. Rev. B 10, 2512.
- Bischoff, H., B. Pilawa, A. Kasten and H.G. Kahle, 1991, J. Phys.: Condens. Matter 3, 10057.
- Blackstead, H.A., 1993, Phys. Rev. B 47, 11411.
- Bleaney, B., 1980, Proc. R. Soc. London Ser. A 370, 313.
- Bleaney, B., 1988, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 11, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam) ch. 77.
- Bleaney, B., 1990, J. Phys.: Condens. Matter 2, 7265.
- Bleaney, B., 1991, Proc. R. Soc. London Ser. A 433, 461.

- Bleaney, B., and M.R. Wells, 1980, Proc. R. Soc. London Ser. A 370, 131.
- Bleaney, B., F.N.H. Robinson, S.H. Smith and M.R. Wells, 1977, J. Phys. C 10, L385.
- Bleaney, B., R.T. Harley, J.F. Ryan, M.R. Wells and M.C.K. Wiltshire, 1978a, J. Phys. C 11, 3059.
- Bleaney, B., F.N.H. Robinson and M.R. Wells, 1978b, Proc. R. Soc. London Ser. A **362**, 179.
- Bleaney, B., A.G. Stephen, Sung Ho Choh and M.R. Wells, 1981a, Proc. R. Soc. London Ser. A 376, 253.
- Bleaney, B., A.G. Stephen, P.J. Walker and M.R. Wells, 1981b, Proc. R. Soc. London Ser. A 376, 235.
- Bleaney, B., J.F. Gregg, A.C. DeOliveira and M.R. Wells, 1982a, J. Phys. C 15, 5293.
- Bleaney, B., A.C. DeOliveira and M.R. Wells, 1982b, J. Phys. C 15, 5275.
- Bleaney, B., A.G. Stephen, P.J. Walker and M.R. Wells, 1982c, Proc. R. Soc. London Ser. A **381**, 1.
- Bleaney, B., G.A. Briggs, J.F. Gregg, G.H. Swallow and J.M.R. Weaver, 1983a, Proc. R. Soc. London Ser. A 388, 479.
- Bleaney, B., J.F. Gregg, M.J.M. Leask and M.R. Wells, 1983b, J. Magn. & Magn. Mater. **31–34**, 1061.
- Bleaney, B., J.H.T. Pasman and M.R. Wells, 1983c, Proc. R. Soc. London Ser. A 387, 75.
- Bleaney, B., R.G. Clark, J.F. Gregg, Y. Roinel and N.J. Stone, 1987, J. Phys. C 20, 3175.
- Bleaney, B., G.A. Briggs, J.F. Gregg, C.H.A. Huan, I.D. Morris and M.R. Wells, 1988a, Proc. R. Soc. London Ser. A 416, 93.
- Bleaney, B., J.F. Gregg, P.C. Hansen, C.H.A. Huan, M. Lazzouni, M.J.M. Leask, I.D. Morris and M.R. Wells, 1988b, Proc. R. Soc. London Ser. A 416, 63.
- Bleaney, B., J.F. Gregg, R.W. Hill, M. Lazzouni, M.J.M. Leask and M.R. Wells, 1988c, J. Phys. C 21, 2721.
- Bleaney, B., M.J.M. Leask, M.G. Robinson, M.R. Wells and C.A. Hutchison Jr, 1990, J. Phys.: Condens. Matter 2, 2009.
- Bleaney, B., R.W. Hill, M.J.M. Leask and M.R. Wells, 1992, J. Magn. & Magn. Mater. 104–107, Part II, 1245.
- Bleaney, B., J.B. Forsyth, M.J.M. Leask, T.M. Mason, R.C.C. Ward and M.R. Wells, 1995, J. Phys. Condens. Matter 7, 1191.
- Bloch, F., 1946, Phys. Rev. 70, 460.
- Bloembergen, N., E.M. Purcell and R.V. Pound, 1948, Phys. Rev. 73, 679.
- Blöte, H.W.J., R.F. Wielinga and W.J. Huiskamp, 1969, Physica 43, 549.
- Blumberg, W.E., 1960, Phys. Rev. 119, 79.
- Bogomolova, G.A., L.A. Bumagina, A.A. Kaminskii and B.Z. Malkin, 1977, Fiz. Tverd. Tela 19, 2439 [Sov. Phys.-Solid State 19, 1428].
- Bohm, W., H.G. Kahle and W. Wuchner, 1984, Phys. Status Solidi (b) 126, 381.
- Bondar', I.A., B.G. Vekhter, Z.A. Kazei, M.D. Kaplan, L.P. Mezentsceva and V.I. Sokolov, 1988, Zh. Eksp. Teor. Fiz. 94, 288 [Sov. Phys.-JETP 67, 1460].
- Bonrath, H., K.H. Hellwege, K. Nicolay and G. Weber, 1966a, Phys. Kondens. Mater. 4, 382.
- Bonrath, H., K.H. Hellwege, S. Hufner, M. Schinkmann, H. Schuchert and G. Weber, 1966b, Phys. Kondens. Mater. 4, 391.
- Bonsall, L., and R.L. Melcher, 1976, Phys. Rev. B 14, 1128.
- Borghini, M., 1966, Phys. Rev. Lett. 16, 318.
- Born, M., and K. Huang, 1954, Dynamical Theory of Crystal Lattices (Clarendon Press, Oxford).
- Bradbury, M.I., and D.J. Newman, 1968, Chem. Phys. Lett. 2, 495.
- Braunisch, W., N. Knauf, V. Kataev, S. Neuhausen, A. Grutz, A. Kock, B. Roden, D. Khomskii and D. Wohlleben, 1992, Phys. Rev. Lett. 68, 1908.
- Bredikhin, S.I., G.A. Emel'chenko, V.Sh. Shekhtman, A.A. Zhokhov, S. Carter, R.J. Chater, J.A. Kilner and B.C.H. Steele, 1991, Physica C 179, 286.
- Brezin, E., 1975, J. Phys. (Paris) Lett. 36, L51.
- Brierley, S.K., and J.A. Griffin, 1982, J. Appl. Phys. 53, 7951.
- Brinkmann, D., and M. Mali, 1994, NMR Basic Principles and Progress, Vol. 31 (Springer, Berlin) pp. 171–211.
- Brinkmann, J., R. Courths and H.J. Guggenheim, 1978, Phys. Rev. Lett. 40, 1286.
- Broach, R.W., J.M. Williams, G.P. Felcher and D.G. Hinks, 1979, Acta Crystallogr. B 35, 2317.
- Brom, H., and H. Alloul, 1991, Physica C 185–189, 1789.
- Brown, P.J., J.B. Forsyth, P.C. Hansen, M.J.M. Leask, R.C.C. Ward and M.R. Wells, 1990, J. Phys.: Condens. Matter 2, 4471.
- Bucher, E., H.J. Guggenheim, K. Andres, G.W. Hull Jr and A.S. Cooper, 1974, Phys. Rev. B 10, 2945.
- Bulaevskii, L.N., J.R. Clem, L.I. Glasman and A.P. Malozemoff, 1992, Phys. Rev. B 45, 2545.
- Bulman, J.B., M.V. Kuric, R.P. Guertin, S. Foner, E.J. McNiff Jr, G. Cao, J. O'Riely, J.E. Crow and P.P. Wise, 1991, J. Appl. Phys. 69, 4874.

- Bumagina, L.A., B.N. Kazakov, B.Z. Malkin and A.L. Stolov, 1977, Fiz. Tverd. Tela 19, 1073 [Sov. Phys.-Solid State 19, 624].
- Bumagina, L.A., V.I. Krotov, B.Z. Malkin and A.Kh. Khasanov, 1981, Zh. Eksp. Theor. Fiz. 80, 1543 [Sov. Phys.-JETP 53, 792].
- Burshtein, A.I., 1968, Kvantovaya Kinetika, Part 1 (Publ. Univ. Novosibirsk, Novosibirsk).
- Cannelli, G., R. Cantelli, F. Cordero, M. Ferretti and L. Verdini, 1990, Phys. Rev. B 42, 7925.
- Capel, H.W., 1965, Physica 31, 1152.
- Carretta, P., and M. Corti, 1992, Phys. Rev. Lett. 68, 1236.
- Cashion, J.D., A.H. Cooke, M.J.M. Leask, T.L. Thorp and M.R. Wells, 1968, J. Mater. Sci. 3, 402.
- Cashion, J.D., A.H. Cooke, T.L. Thorp and M.R. Wells, 1970, Proc. R. Soc. London Ser. A, **318**, 473.
- Catanese, C.A., A.T. Skjeltorp, H.E. Meissner and W.P. Wolf, 1973, Phys. Rev. B 8, 4223.
- Cava, R.J., A.W. Hewat, B. Batlogg, M. Marezio, K.M. Rable, J.J. Krajewski, W.F. Peck Jr and L.W. Rupp Jr, 1990, Physica C 165, 419.
- Chan, K.S., 1985, J. Phys. C 18, 1677.
- Chan, K.S., S.C. Chen and D.J. Newman, 1984, J. Phys. C 17, 3049.
- Chapellier, M., M. Goldman, Vu Hoang Chau and A. Abragam, 1969, C. R. Acad. Sci. Ser. B 268, 1530.
- Christensen, H.P., 1978, Phys. Rev. B 17, 4060.
- Christensen, H.P., 1979a, Phys. Rev. B 19, 6564.
- Christensen, H.P., 1979b, Phys. Rev. B 19, 6573.
- Chrosch, J., and E.K.H. Salje, 1994, Physica C 225, 111.
- Clark, R.G., A.L. Allsop, N.J. Stone and G.J. Bowden, 1987, J. Phys. C 20, 797.
- Claus, H., U. Gebhard, G. Linker, K. Röhberg, S. Riedling, J. Franz, T. Ishida, A. Erb, G. Müller-Vogt and H. Wühl, 1992, Physica C 200, 271.
- Clinton, T.W., J.W. Lynn, J.Z. Liu, Y.X. Jia and R.N. Shelton, 1991, J. Appl. Phys. 70, 5751.
- Clinton, T.W., J.W. Lynn, B.W. Lee, M. Buchgeister and M.B. Maple, 1993, J. Appl. Phys. 73, 6320.
- Clinton, T.W., J.W. Lynn, J.Z. Liu, Y.X. Jia, T.J. Goodwin, R.N. Shelton, B.W. Lee, M. Buchmeister, M.B. Maple and J.L. Peng, 1995, Phys. Rev. B 51, 15429.
- Cochrane, R.W., C.Y. Wu and W.P. Wolf, 1973, Phys. Rev. B 8, 4348.
- Cohen, E., L.A. Riseberg, W.A. Nordland, R.D. Burbank, R.C. Sherwood and L.G. Van Uitert, 1969, Phys. Rev. 186, 476.

- Cohen, E., M.D. Sturge, R.J. Birgeneau, E.I. Blount, L.G. Van Uitert and J.K. Kjems, 1974, Phys. Rev. Lett. 33, 232.
- Cohen, M.H., and F. Keffer, 1955, Phys. Rev. 99, 1135.
- Colwell, J.H., B.W. Mangum and D.B. Utton, 1969, Phys. Rev. 181, 842.
- Colwell, J.H., B.W. Mangum and D.D. Thornton, 1971, Phys. Rev. B **3**, 3855.
- Cone, R.L., and W.P. Wolf, 1978, Phys. Rev. B 17, 4162.
- Cooke, A.H., D.T. Edmonds, C.B.P. Finn and W.P. Wolf, 1968, Proc. R. Soc. London Ser. A 306, 313, 335.
- Cooke, A.H., D.M. Martin and M.R. Wells, 1971, J. Phys. (Paris) Suppl. 32, C1-645.
- Cooke, A.H., S.J. Swithenby and M.R. Wells, 1973, J. Phys. C 6, 2209.
- Cooke, A.H., D.A. Jones, J.F.A. Silva and M.R. Wells, 1975, J. Phys. C 8, 4083.
- Cooke, A.H., M.M. Davidson, N.J. England, M.J.M. Leask, J.B. Lowry, A.C. Tropper and M.R. Wells, 1976, J. Phys. C 9, L573.
- Cooper, S.L., D. Reznik, A. Kotz, M.A. Karlow, R. Liu, M.V. Klein, W.C. Lee, J. Giapintzakis and D.M. Ginsberg, 1993, Phys. Rev. B 47, 8233.
- Corruccini, L.R., and S.J. White, 1993, Phys. Rev. B 47, 773.
- Corruccini, L.R., S.J. White and M.R. Roser, 1994, Physica B 194–196, 281.
- Dahl, M., and G. Schaack, 1986, Phys. Rev. Lett. 56, 232.
- Davidova, M.P., S.B. Zdanovitch, B.N. Kazakov, S.L. Korableva and A.L. Stolov, 1977, Opt. Spectrosk. 42, 577.
- Davidova, M.P., B.N. Kazakov and A.L. Stolov, 1978, Fiz. Tverd. Tela 20, 2391 [Sov. Phys.-Solid State 20, 1378].
- de Groot, P., F. Leempoels, J. Witters, F. Herlach and I. Laursen, 1981, Solid State Commun. 37, 681.
- De'Bell, K., and J.P. Whitehead, 1991, J. Phys.: Condens. Matter 3, 2431.
- Deutscher, G., and K.A. Müller, 1987, Phys. Rev. Lett. 59, 1745.
- Dick, B.G., and A. Overhauser, 1958, Phys. Rev. 112, 90.
- D'Iorio, M., W. Berlinger, J.G. Bednorz and K.A. Muller, 1984, J. Phys. C 17, 2293.
- Dirkmaat, A.J., D. Huser, G.J. Nieuwenhuys, J.A. Mydosh, P. Kettler and M. Steiner, 1987, Phys. Rev. B 36, 352.

Dohm, V., and P. Fulde, 1975, Z. Phys. B 21, 369.

- Dooglav, A.V., A.V. Egorov, H. Lütgemeier, O.V. Marvin, M.A. Teplov and D. Wagener, 1992, in: Proc. 5th Bilateral Russian–German Seminar on High-T_c Superconductivity, October 4–8, 1992, Kloster Banz, Germany.
- Dorfler, W., and G. Schaack, 1985, Z. Phys. B 59, 283.
- Dunlap, B.D., M. Slaski, D.G. Hinks, L. Soderholm, M. Beno, K. Zhang, C. Segre, G.W. Crabtree, W.K. Kwok, S.K. Malik, I.K. Schuller, J.D. Jorgensen and Z. Sungaila, 1987, J. Magn. & Magn. Mater. 68, L139.
- Edwards, H.L., J.T. Markert and A.L. de Lozanne, 1992, Phys. Rev. Lett. 69, 2967.
- Egorov, A.V., M.V. Eremin, M.S. Tagirov and M.A. Teplov, 1979, Zh. Eksp. Teor. Fiz. 77, 2375.
- Egorov, A.V., L.D. Livanova, M.S. Tagirov and M.A. Teplov, 1980, Fiz. Tverd. Tela 22, 2836.
- Egorov, A.V., F.L. Aukhadeev, M.S. Tagirov and M.A. Teplov, 1984a, Zh. Eksp. Teor. Fiz. Pis'ma Red. 39, 480.
- Egorov, A.V., A.A. Kudryashov, M.S. Tagirov and M.A. Teplov, 1984b, Fiz. Tverd. Tela 26, 2223.
- Egorov, A.V., H. Lütgemeier, D. Wagener, A.V. Dooglav and M.A. Teplov, 1992, Solid State Commun. 83, 111.
- Ellingsen, O.S., H. Bratsberg, S. Mroczkowski and A.T. Skjeltorp, 1982, J. Appl. Phys. 53, 7948.
- Elliott, R.J., R.T. Harley, W. Hayes and S.R.P. Smith, 1972, Proc. R. Soc. London Ser. A 328, 217.
- Elmaleh, D., D. Fruchart and J.C. Joubert, 1971, J. Phys. (Paris), Suppl. 32, C1-741.
- Emerson, J.P., R.A. Fisher, N.E. Phillips, D.A. Wright and E.M. McCarron III, 1994, Phys. Rev. B 49, 9256.
- Emery, V.J., and S.A. Kivelson, 1993, Physica C 209, 597.
- Emery, V.J., S.A. Kivelson and H.Q. Lin, 1990, Phys. Rev. Lett. 64, 475.
- Enderle, M., B. Pilawa, W. Schlaphot and H.G. Kahle, 1990a, J. Phys.: Condens. Matter 2, 4685.
- Enderle, M., B. Pilawa, M. Schwab and H.G. Kahle, 1990b, J. Phys.: Condens. Matter 2, 4701.
- Erath, E.H., 1961, J. Chem, Phys. 34, 1985.
- Erdos, P., and J.H. Kang, 1972, Phys. Rev. B 6, 3393.
- Eremin, M.V., 1989, in: Spectroscopy of Crystals, ed. A.A. Kaplyanskii (Science, Leningrad) pp. 30–44.
- Eremin, M.V., and E. Sigmund, 1994, Solid State Commun. 90, 795.

- Eremin, M.V., I.S. Konov and M.A. Teplov, 1977, Zh. Eksp. Teor. Fiz. 73, 569.
- Eremin, M.V., I.N. Kurkin, M.P. Rodionova, I.Kh. Salikhov, L.L. Sedov and L.R. Tagirov, 1991, Supercond. Phys. Chem. Techn. 4, 716.
- Faucher, M., and D. Garcia, 1982, Phys. Rev. B 26, 5451.
- Favorskii, I.A., 1985, Fiz. Nizk. Temp. (Kiev) 11, 736 [Sov. J. Low Temp. Phys. 11, 404].
- Felsteiner, J., 1970, J. Phys. C 3, L174.
- Felsteiner, J., and Z. Friedman, 1973, Phys. Rev. B 7, 1078.
- Felsteiner, J., and S.K. Misra, 1973, Phys. Rev. B 8, 253.
- Feuss, H., and A. Kallel, 1972, J. Solid State Chem. 5, 11.
- Filippi, J., J.C. Lasjaunias, B. Hebral, J. Rossat-Mignod and F. Tcheou, 1980, J. Magn. & Magn. Mater. 15– 18, 527.
- Fillion, G., D. Cox, R. Kurtz, N. Giordano and W.P. Wolf, 1980, J. Magn. & Magn. Mater. 15-18, 23.
- Fish, G.E., and H.J. Stapleton, 1978, J. Chem. Phys. 69, 4068.
- Fitzwater, D.R., and R.E. Rundle, 1959, Z. Kristallogr. 112, 362.
- Folinsbee, J.T., J.P. Harrison, D.B. McColl and D.R. Taylor, 1977a, J. Phys. C 10, 743.
- Folinsbee, J.T., P.R. Tapster, D.R. Taylor, S. Mroczkowski and W.P. Wolf, 1977b, Solid State Commun. 24, 499.
- Folkins, J.J., J.A. Griffin and D.U. Gubser, 1982, Phys. Rev. B 25, 405.
- Folle, H.R., M. Kubota, C. Buchal, R.M. Mueller and F. Pobell, 1981, Z. Phys. B 41, 223.
- Fontaine, D., L.T. Wille and S.C. Moss, 1987, Phys. Rev. B 36, 5709.
- Fontaine, D., G. Ceder and M. Asta, 1990, J. Less-Common Met. 164–165, 108.
- Freeman, A.J., and J.P. Desclaux, 1979, J. Magn. & Magn. Mater. 12, 11.
- Freeman, A.J., and R.E. Watson, 1962, Phys. Rev. 127, 2058.
- Frey, E., and F. Schwabl, 1990, Phys. Rev. B 42, 8261.
- Frowein, R., and J. Kotzler, 1976, Z. Phys. B 25, 279.
- Frowein, R., J. Kotzler and W. Assmus, 1979, Phys. Rev. Lett. **42**, 739.
- Frowein, R., J. Kotzler, B. Schaub and H. Schuster, 1982, Phys. Rev. B 25, 4905.
- Furrer, A., P. Bruesch and P. Unternahrer, 1988, Phys. Rev. B **38**, 4616.

- Garcia, D., and M. Faucher, 1983, J. Less-Common Met. 93, 119.
- Garcia, D., and M. Faucher, 1985, J. Chem. Phys. 82, 5554.
- Garcia, D., and M. Faucher, 1995, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 21, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam) p. 263.
- Gehring, G.A., and K.A. Gehring, 1975, Rep. Progr. Phys. 38, 1.
- Gehring, G.A., H.G. Kahle, W. Nagele, A. Simon and W. Wuchner, 1976a, Phys. Status Solidi (b) 74, 297.
- Gehring, G.A., S.J. Swithenby and M.R. Wells, 1976b, Solid State Commun. 18, 31.
- Glynn, T.J., R.T. Harley, W. Hayes and A.J. Rushworth, 1975, J. Phys. C 8, L126.
- Glynn, T.J., R.T. Harley and R.M. Macfarlane, 1977, J. Phys. C 10, 2937.
- Goto, T., A. Tamaki, T. Fujimura and H. Unoki, 1986, J. Phys. Soc. Jpn. 55, 1613.
- Graf, T., G. Triscone and J. Muller, 1990, J. Less-Common Met. 159, 349.
- Graham, J.T., M. Maliepaard, J.H. Page, S.R.P. Smith and D.R. Taylor, 1987, Phys. Rev. B 35, 2098.
- Graham, J.T., D.R. Taylor, D.R. Noakes and W. Buyers, 1991a, Phys. Rev. B 43, 3778.
- Graham, J.T., J.H. Page and D.R. Taylor, 1991b, Phys. Rev. B 44, 4127.
- Grahl, M., and J. Kotzler, 1989, Z. Phys. B 75, 527.
- Griffin, J.A., and J.D. Litster, 1979, Phys. Rev. B 19, 3676.
- Griffin, J.A., M. Huster and R.J. Folweiler, 1980, Phys. Rev. B 22, 4370.
- Griffin, J.A., J.J. Folkins and D. Gabbe, 1981, Phys. Rev. B 24, 6516.
- Griffiths, J.S., 1963, Phys. Rev. 132, 316.
- Grohmann, I., K.H. Hellwege and H.G. Kahle, 1961, Z. Physik 164, 243.
- Guan, W.Y., Y.C. Chen, J. Wei, Y.H. Hu and M.K. Wu, 1993, Physica C 209, 19.
- Guillaume, M., P. Allenspach, J. Mesot, U. Staub, A. Furrer, H. Mutka, R. Osborn, A. Taylor, F. Stucki and P. Unternahrer, 1992, Solid State Commun. 81, 999.
- Guillaume, M., P. Allenspach, J. Mesot, B. Roessli, U. Staub, P. Fischer and A. Furrer, 1993, Z. Phys. B 90, 13.
- Guttmann, A.J., 1975, J. Phys. C 8, 4056.
- Hadjiev, V.G., C. Thomsen, J. Kircher and M. Cardona, 1993, Phys. Rev. B 47, 9148.

- Halbritter, J., 1993, Phys. Rev. B 48, 9735.
- Ham, F.S., 1965, Phys. Rev. A 138, 1727.
- Hammann, J., and P. Manneville, 1973, J. Phys. (Paris) 34, 615.
- Hammann, J., and M. Ocio, 1977, Physica B 86-88, 1153.
- Hammann, J., and M. Ocio, 1980, J. Magn. & Magn. Mater. 15–18, 39.
- Hansen, P.E., and R. Nevald, 1977, Phys. Rev. B 16, 146.
- Harley, R.T., 1987, in: Spectroscopy of Solids Containing Rare-Earth Ions, eds A.A. Kaplyanskii and R.M. Macfarlane (Elsevier Science Publishers, Amsterdam) p. 557.
- Harley, R.T., and D.I. Manning, 1978, J. Phys. C 11, L633.
- Harley, R.T., W. Hayes, A.M. Perry and S.R.P. Smith, 1973, J. Phys. C 6, 2382.
- Harley, R.T., W. Hayes, A.M. Perry, S.R.P. Smith, R.J. Elliott and I.D. Saville, 1974, J. Phys. C 7, 3145.
- Harley, R.T., W. Hayes, A.M. Perry and S.R.P. Smith, 1975, J. Phys. C 8, L123.
- Harrison, J.P., J.P. Hessler and D.R. Taylor, 1976, Phys. Rev. B 14, 2979.
- Hawkes, J.F.B., and M.J.M. Leask, 1972, J. Phys. C 5, 1705.
- Heinmaa, I., H. Lütgemeier, S. Pekker, G. Krabbes and M. Buchgeister, 1992, Appl. Magn. Reson. 3, 689.
- Hellwege, K.H., and J.W. Stout, 1968, J. Appl. Phys. 39, 1137.
- Henry, W.E., 1955, Phys. Rev. 98, 226.
- Hess, G., M. Dommann, H.G. Kahle, A. Kasten, C. Seifert and K. Vogtlin, 1990, J. Phys.: Condens. Matter 2, 1073.
- Hirvonen, M.T., T.E. Katila, K.J. Riski, M.A. Teplov, B.Z. Malkin, N.E. Phillips and M. Wun, 1975, Phys. Rev. B 11, 4652.
- Hodges, J.A., 1975a, Solid State Commun. 17, 919.
- Hodges, J.A., 1975b, Phys. Status. Solidi (b) 68, K73.
- Hodges, J.A., 1977, Physica B 86-88, 1143.
- Hodges, J.A., 1978, J. Phys. C 11, 1651.
- Hodges, J.A., 1983a, Hyperfine Int. 15/16, 767.
- Hodges, J.A., 1983b, J. Phys. (Paris) 44, 833.
- Hodges, J.A., 1985, J. Phys. C 18, 4373.
- Hodges, J.A., P. Imbert and G. Jehanno, 1982, J. Phys. (Paris) **43**, 1249.
- Hodges, J.A., P. Imbert and G. Jehanno, 1987, Solid State Commun. 64, 1209.

- Hodges, J.A., P. Bonville, P. Imbert and G. Jehanno, 1991a, Physica C 184, 259.
- Hodges, J.A., P. Bonville, P. Imbert, G. Jehanno and P. Debray, 1991b, Physica C 184, 270.
- Holmes, L.M., H.J. Guggenheim and G.W. Hull Jr, 1970, Solid State Commun. 8, 2005.
- Holmes, L.M., J. Als-Nielsen and H.J. Guggenheim, 1975, Phys. Rev. B 12, 180.
- Holstein, T., and H. Primakoff, 1940, Phys. Rev. 58, 1098.
- Horiuchi, S., 1992, Jpn. J. Appl. Phys. 31, L1335.
- Horvitz, E.P., 1971, Phys. Rev. B 3, 2868.
- Hulsing, H., and A. Kasten, 1979, J. Magn. & Magn. Mater. 13, 156.
- Hulsing, H., H.G. Kahle, M. Schwab and H.J. Schwarzbauer, 1978, J. Magn. & Magn. Mater. 9, 68.
- Hulsing, H., H.G. Kahle and A. Kasten, 1980, J. Magn. & Magn. Mater. 15–18, 512.
- Hulsing, H., H.G. Kahle and A. Kasten, 1983, J. Magn. & Magn. Mater. **31–34**, 1073.
- Hundley, M.F., J.D. Thompson, S.-W. Cheong and Z. Fisk, 1989, Physica C 158, 102.
- Hutchings, M.T., 1964, Solid State Phys. 16, 227.
- Hutchings, M.T., and W.P. Wolf, 1963, Phys. Rev. Lett. 11, 187.
- Hutchings, M.T., C.G. Windsor and W.P. Wolf, 1966, Phys. Rev. 148, 444.
- Hutchings, M.T., R.J. Birgeneau and W.P. Wolf, 1968, Phys. Rev. 168, 1026.
- Ihringer, J., 1982, Solid State Commun. 41, 525.
- Iliev, M., C. Thomsen, V.G. Hadjiev and M. Cardona, 1993, Phys. Rev. B 47, 12341.
- Ioffe, V.A., S.I. Andronenko, I.A. Bondar', L.P. Mezentsceva, A.N. Bazhan and C. Bazan, 1981, Zh. Eksp. Teor. Fiz. Pis'ma Red. 34, 586.
- Ioffe, V.A., S.I. Andronenko, A.N. Bazhan, S.V. Kravchenko, C. Bazan, B.G. Vekhter and M.D. Kaplan, 1983, Zh. Eksp. Teor. Fiz. 84, 707.
- Ishigaki, T., K. Mori, O.N. Bakharev, A.V. Dooglav, E.V. Krjukov, O.V. Lavizina, O.V. Marvin, I.R. Mukhamedshin and M.A. Teplov, 1995, Solid State Commun. 96, 465.
- Ishimoto, H., N. Nishida, T. Furubayashi, M. Shinomara, Y. Takano, Y. Miora and K. Ono, 1984, J. Low Temp. Phys. 55, 17.
- Islam, M.S., and R.C. Baetzold, 1994, J. Mater. Chem. 4, 299.
- Ivanov, M.A., V.Ya. Mitrofanov, L.D. Falkovskaya and A.Ya. Fishman, 1983, J. Magn. & Magn. Mater. 36, 26.

- Janssen, P., P. de Groot and L. Van Bockstal, 1983, J. Magn. & Magn. Mater. 31-34, 687.
- Janssen, P., I. de Wolf and I. Laursen, 1985, J. Phys. & Chem. Solids 46, 1387.
- Jensen, S.J.K., and K. Kjaer, 1989, J. Phys.: Condens. Matter 1, 2361.
- Jones, E.D., 1967, Phys. Rev. Lett. 19, 432.
- Jones, E.D., 1968, J. Phys. & Chem. Solids 29, 1305.
- Jones, E.D., and V.H. Schmidt, 1969, J. Appl. Phys. 40, 1406.
- Jørgensen, C.K., R. Pappalardo and H.-H. Schmidtke, 1963, J. Chem. Phys. 39, 1422.
- Jorgensen, J.D., Shiyou Pei, P. Lightfoot, H. Shi, A.P. Paulikas and B.W. Veal, 1990a, Physica C 167, 571.
- Jorgensen, J.D., B.W. Veal, A.P. Paulikas, L.J. Nowicki, G.W. Crabtree, H. Claus and W.K. Kwok, 1990b, Phys. Rev. B 41, 1863.
- Jorgensen, J.D., D.G. Hinks, P.G. Radaelli, Shiyou Pei, P. Lightfoot, B. Dabrowski, C.U. Segre and B.A. Hunter, 1991, Physica C 185, 184.
- Judd, B.R., and I. Lindgren, 1961, Phys. Rev. 122, 1802.
- Kahle, H.G., and A. Kasten, 1983, J. Magn. & Magn. Mater. 31–34, 1081.
- Kahle, H.G., L. Klein, G. Miller-Vogt and H.C. Schopper, 1971, Phys. Status Solidi (b) 44, 619.
- Kaminskii, A.A., 1975, Lazernye Kristally (Nauka, Moscow) p. 256.
- Kaplan, M.D., and B.G. Vekhter, 1983, J. Phys. C 16, L191.
- Kappatsch, A., S. Quezel-Ambrunaz and J. Sivardiere, 1970, J. Phys. (Paris) 31, 369.
- Kasten, A., 1980, Z. Phys. B 38, 65.
- Kasten, A., and H.G. Kahle, 1986, J. Magn. & Magn. Mater. 54–57, 1325.
- Kasten, A., P. Berndts and H.G. Kahle, 1975, Physica B 80, 258.
- Kasten, A., H.G. Kahle, P. Klofer and D. Schafer-Siebert, 1987, Phys. Status Solidi (b) 144, 423.
- Katila, T.E., V.K. Typpi and E.R. Seidel, 1970, in: Proc. 12th Int. Conf. on Low Temperature Physics, Kyoto, 1970, pp. 711–713.
- Katila, T.E., N.E. Phillips, M.C. Veuro and B.B. Triplett, 1972, Phys. Rev. B 6, 1827.
- Kazei, Z.A., and N.P. Kolmakova, 1993, Zh. Eksp. Teor. Fiz. 103, 316 [Sov. Phys.-JETP 76, 172].
- Kazei, Z.A., and V.I. Sokolov, 1986, Zh. Eksp. Teor. Fiz. 91, 1799 [Sov. Phys.-JETP 64, 1065].
- Kazei, Z.A., N.P. Kolmakova, P. Novak and V.I. Sokolov, 1991, Garnets, Landolt-Bornstein New

Series, Group III, Crystal and Solid State Physics, Vol. 27, subvol. e (Springer, Berlin).

- Ketelaar, J.A.A., 1939, Physica 4, 619.
- Khachaturyan, A.G., and J. Morris Jr, 1987, Phys. Rev. Lett. 59, 2776.
- Khat'sko, E.N., A.S. Cherny, M.I. Kobetz and V.A. Paschenko, 1994, Fiz. Nizk. Temp. (Kiev) 20, 1022.
- Khutsishvili, G.R., 1968, Usp. Fiz. Nauk. 96, 441.
- Kikuchi, R., and J.S. Choi, 1989, Physica C 160, 347.
- King, A.R., J.P. Wolfe and R.L. Ballard, 1972, Phys. Rev. Lett. 28, 1099.
- Kittel, C., 1949, Rev. Mod. Phys. 21, 541.
- Kivelson, S.A., V.J. Emery and H.Q. Lin, 1990, Phys. Rev. B 42, 6523.
- Kjaer, K., J. Als-Nielsen, I. Laursen and F. Krebs Larsen, 1989, J. Phys.: Condens. Matter 1, 5743.
- Klafter, J., and A. Blumen, 1984, J. Chem. Phys. 80, 875.
- Klauder, J.R., and P.W. Anderson, 1962, Phys. Rev. 125, 912.
- Kleiner, R.K., and P. Muller, 1994, Phys. Rev. B 49, 1327.
- Knoll, K.D., 1971, Phys. Status Solidi (b) 45, 553.
- Kockelmann, W., W. Schäfer and G. Will, 1991, Eur. J. Sol. State. Inorg. Chem. 28, Suppl., 515.
- Kolmakova, N.P., I.B. Krynetskii, M.M. Lukina and A.A. Mukhin, 1990, Phys. Status Solidi (b) 159, 845.
- Konov, I.S., and M.A. Teplov, 1976a, Fiz. Tverd. Tela 18, 853.
- Konov, I.S., and M.A. Teplov, 1976b, Fiz. Tverd. Tela 18, 1114.
- Konov, I.S., and M.A. Teplov, 1977, Fiz. Tverd. Tela 19, 285.
- Korableva, S.L., I.N. Kurkin, S.V. Lukin and K.P. Chernov, 1982, Fiz. Tverd. Tela 24, 1235.
- Korableva, S.L., M.S. Tagirov and M.A. Teplov, 1983, Paramagnitnii Rezonans, No. 16 (Publ. University Kazan) p. 7.
- Kostetskii, Yu.Yu., 1988, Ref. Zh. Fiz. 18E 10E188 Dep.
- Kotzler, J., 1980, J. Magn. & Magn. Mater. 15-18, 393.
- Kotzler, J., D. Sellmann and W. Aszmus, 1984, J. Magn. & Magn. Mater. 45, 245.
- Krauns, C., and H.-U. Krebs, 1993, Z. Phys. B 92, 43.
- Krekels, T., H. Zou, G. Van Tendeloo, D. Wagener, M. Buchgeister, S.M. Hosseini and P. Herzog, 1992, Physica C 196, 363.

- Kristofel', N.N., 1974, Teoriya Primesnikh Tsentrov Malykh Radiusov v lonnykh Kristallakh (Nauka, Moscow) p. 336.
- Krjukov, E.V., O.V. Marvin, E.A. Semenova, M.A. Teplov, K.M. Enikeev and A.V. Klochkov, 1994, Zh. Eksp. Teor. Fiz. Pis'ma Red. 60, 30 [JETP Lett. 60, 30].
- Krotov, V.I., B.Z. Malkin and A.A. Mittel'man, 1982, Fiz. Tverd. Tela 24, 542.
- Krygin, I.M., and A.D. Prokhorov, 1984, Zh. Eksp. Teor. Fiz. 86, 590.
- Kubo, Y., and H. Igarashi, 1989, Phys. Rev. B 39, 725.
- Kubota, M., R.M. Mueller, Ch. Buchal, H. Chocholaes, J.R. Owers-Bradley and F. Pobell, 1983, Phys. Rev. Lett. 51, 1382.
- Kupchikov, A.K., B.Z. Malkin, D.A. Rzaev and A.I. Ryskin, 1982, Fiz. Tverd. Tela 24, 2373 [Sov. Phys.-Solid State 24, 1348].
- Kupchikov, A.K., B.Z. Malkin, A.L. Natadze and A.I. Ryskin, 1987, Fiz. Tverd. Tela 29, 3335.
- Kurkin, I.N., I.Kh. Salikhov, L.L. Sedov, M.A. Teplov and R.Sh. Zhdanov, 1993, Zh. Eksp. Teor. Fiz. 103, 1342 [Sov. Phys.-JETP, 76, 657].
- Kurti, N., N.H.F. Robinson, F.E. Simon and D.A. Spohr, 1956, Nature 178, 450.
- Lagendijk, E., H.W.J. Blöte and W.J. Huiskamp, 1972, Physica 61, 220.
- Landau, D.P., J.C. Doran and B.E. Keen, 1973, Phys. Rev. B 7, 4961.
- Larkin, I.A., and D.E. Khmel'nitskii, 1969, Zh. Eksp. Teor. Fiz. 65, 2087 [Sov. Phys.-JETP, 29, 1123].
- Larson, G.H., and C.D. Jeffries, 1966a, Phys. Rev. 141, 461.
- Larson, G.H., and C.D. Jeffries, 1966b, Phys. Rev. 145, 311.
- Laugsch, J., H.G. Kahle, M. Schwab and W. Wuchner, 1975, Physica B 80, 269.
- Lavrov, A.N., 1992, Phys. Lett. A 168, 71.
- Leask, M.J.M., A.C. Tropper and M.R. Wells, 1981, J. Phys. C 14, 3481.
- Leask, M.J.M., M.R. Wells, R.C.C. Ward, S.M. Hayden and J. Jensen, 1994, J. Phys.: Condens. Matter 6, 505.
- Lee, W.C., K. Sun, L.L. Miller, D.C. Johnston, R.A. Klemm, S. Kim, R.A. Fisher and N.E. Phillips, 1991, Phys. Rev. B 43, 463.
- Lines, M.E., 1974, Phys. Rev. B 9, 950.
- Lloyd, R.G., and P.W. Mitchell, 1990, J. Phys.: Condens. Matter 2, 2383.

- Lohmuller, G., G. Schmidt, B. Deppish, V. Gramlich and C. Scheringer, 1973, Acta Crystallogr. B 29, 141.
- Loong, C.-K., L. Soderholm, M.M. Abraham, L.A. Boatner and N.M. Edelstein, 1993a, J. Chem. Phys. 98, 4214.
- Loong, C.-K., L. Soderholm, G.L. Goodman, M.M. Abraham and L.A. Boatner, 1993b, Phys. Rev. B 48, 6124.
- Loong, C.-K., L. Soderholm, J.P. Hammonds, M.M. Abraham, L.A. Boatner and N.M. Edelstein, 1993c, J. Phys.: Condens. Matter 5, 5121.
- Lütgemeier, H., I. Heinmaa and A.V. Egorov, 1993, Physica Scripta T 49, 137.
- Luttinger, J.M., and L. Tisza, 1946, Phys. Rev. 70, 954.
- Lynn, J.W., 1992, J. Alloys & Compounds 180, 419.
- Lyons, K.B., R.J. Birgeneau, E.I. Blount and L.G. Van Uitert, 1975, Phys. Rev. B 11, 891.
- MacChesney, J.B., H.J. Williams and R.C. Sherwood, 1964, J. Chem. Phys. 41, 3177.
- MacChesney, J.B., H.J. Williams, R.C. Sherwood and J.F. Potter, 1966, J. Chem. Phys. 44, 596.
- MacIsaac, A.B., J.P. Whitehead, K. De'Bell and K.S. Narayanan, 1992, Phys. Rev. B 46, 6387.
- Magarino, J., J. Tuchendler and P.E. Hansen, 1978, Physica B 86–88, 1233.
- Magarino, J., J. Tuchendler, P. Beauvillain and I. Laursen, 1980, Phys. Rev. B 21, 18.
- Malhotra, V.M., H.D. Bist and G.C. Upreti, 1977, J. Magn. Reson. 27, 439.
- Malkin, B.Z., 1963, Fiz. Tverd. Tela 5, 3088.
- Malkin, B.Z., 1987, in: Spectroscopy of Solids Containing Rare-Earth Ions, eds A.A. Kaplyanskii and R.M. Macfarlane (Elsevier Science Publishers, Amsterdam) p. 13.
- Malkin, B.Z., Z.I. Ivanenko and I.B. Aizenberg, 1970, Fiz. Tverd. Tela 12, 1873 [Sov. Phys.-Solid State 12, 1491].
- Malkin, B.Z., M.A. Koreiba, V.R. Pekurovskii and A.R. Somov, 1993, Izv. Akad. Nauk SSSR, Ser. Fiz. 57, 19.
- Marchand, R.L., and H.J. Stapleton, 1974, Phys. Rev. 139, 14.
- McHenry, M.R., B.G. Silbernagel and J.H. Wernick, 1972, Phys. Rev. B 5, 2958.
- Mehran, F., and K.W.H. Stevens, 1982, Phys. Rep. 85, 123.
- Mehran, F., T.S. Plaskett and K.W.H. Stevens, 1977, Phys. Rev. B 16, 1.

- Mehran, F., K.W.H. Stevens and T.S. Plaskett, 1979a, Phys. Rev. B 20, 867.
- Mehran, F., K.W.H. Stevens and T.S. Plaskett, 1979b, Phys. Rev. B 20, 1817.
- Mehran, F., K.W.H. Stevens, T.S. Plaskett and W.J. Fitzpatrick, 1980, Phys. Rev. B 22, 2206.
- Mehran, F., K.W.H. Stevens, T.S. Plaskett and W.J. Fitzpatrick, 1982, Phys. Rev. B 25, 1973.
- Mehran, F., K.W.H. Stevens, T.S. Plaskett and W.J. Fitzpatrick, 1983, Phys. Rev. B 27, 548.
- Mehring, M., 1992, Appl. Magn. Reson. 3, 383.
- Melcher, R.L., 1976, in: Physical Acoustics, Vol. 12, eds V.P. Mason and R.N. Thurston (Academic Press, N.Y.) p. 1.
- Mennenga, G., L.J. de Jongh, W.J. Huiskamp and I. Laursen, 1984a, J. Magn. & Magn. Mater. 44, 48.
- Mennenga, G., L.J. de Jongh and W.J. Huiskamp, 1984b, J. Magn. & Magn. Mater. 44, 59.
- Mennenga, G., P.R. Nugteren, L.J. de Jongh, I. Laursen, J.P. Renard and P. Beauvillain, 1985, J. Magn. & Magn. Mater. 53, 264.
- Mensinger, H., J. Jakelski, H.G. Kahle, A. Kasten and W. Paul, 1993, J. Phys.: Condens. Matter 5, 935.
- Mesot, J., P. Allenspach, U. Staub, A. Furrer and H. Mutka, 1993a, Phys. Rev. Lett. 70, 865.
- Mesot, J., P. Allenspach, U. Staub, A. Furrer, H. Mutka, R. Osborn and A. Taylor, 1993b, Phys. Rev. B 47, 6027.
- Metcalfe, M.J., and H.M. Rosenberg, 1972, J. Phys. C 5, 450.
- Metzger, J., T. Weber, W.H. Fietz, K. Grube, H.A. Ludwig, T. Wolf and H. Wuhl, 1993, Physica C 214, 371.
- Misra, S.K., and J. Felsteiner, 1977, Phys. Rev. B 15, 4309.
- Misra, S.K., and J. Felsteiner, 1992, Phys. Rev. B 46, 11033.
- Misra, S.K., and P. Mikolajczak, 1978, J. Chem. Phys. 69, 3093.
- Misra, S.K., and P. Mikolajczak, 1979, J. Phys. & Chem. Solids 40, 477.
- Misra, S.K., and G.R. Sharp, 1976, Phys. Status Solidi (b) **75**, 607.
- Mogilevsky, R., R. Levi-Setti, B. Pashmakov, Li Lin, K. Zhang, H.M. Jaeger, D.B. Buchholz, R.P.H. Chang and B.W. Veal, 1994, Phys. Rev. B 49, 6420.
- Morin, P., and D. Schmitt, 1990, in: Ferromagnetic Materials, Vol. 5, ch. 1, eds K.H.J. Buschow and E.P. Wohlfarth (North-Holland, Amsterdam) pp. 1– 132.

- Morin, P., D. Schmitt and E. Du Tremolet de Lacheisserie, 1980, Phys. Rev. B 21, 1742.
- Morra, R.M., R.L. Armstrong and D.R. Taylor, 1983, Phys. Rev. Lett. 51, 809.
- Morrison, C.A., 1976, Solid State Commun. 18, 153.
- Morrison, C.A., and R.P. Leavitt, 1982, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 5, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam) p. 461.
- Morss, L.R., M. Siegal, L. Stenger and N. Edelstein, 1970, Inorg. Chem. 9, 1771.
- Muller, A.U., J. Jakelski and H.G. Kahle, 1993, J. Phys.: Condens. Matter 5, 955.
- Muller, P.H., A. Kasten and M. Schienle, 1983, Phys. Status Solidi (b) **119**, 239.
- Murao, T., 1983, J. Phys. C 16, 335.
- Murao, T., 1988, J. Phys. (Paris) Suppl. 49, C8-903.
- Muroi, M., and R. Street, 1993a, Physica C 208, 107.
- Muroi, M., and R. Street, 1993b, Physica C 216, 345.
- Mutscheller, W., and M. Wagner, 1986, Phys. Status Solidi (b) **134**, 39.
- Nakajima, T., H. Suzuki and K. Tsutsumi, 1990, Physica B 165–166, 915.
- Nejlo, G.N., and A.D. Prokhorov, 1983, Fiz. Nizk. Temp. (Kiev) 9, 877.
- Neogy, D., A. Chatterji and A. Neogy, 1978, J. Chem. Phys. 69, 2703.
- Nevald, R., and P.E. Hansen, 1978, Phys. Rev. B 18, 4626.
- Newman, D.J., 1971, Adv. Phys. 20, 197.
- Newman, D.J., 1978, Aust. J. Phys. 31, 79.
- Newman, D.J., and B. Ng, 1989, Rep. Progr. Phys. 52, 699.
- Niemeijer, Th., and P.H.E. Meijer, 1974, Phys. Rev. B 10, 2962.
- Osborn, R., and E.A. Goremychkin, 1991, Physica C 185–189, 1179.
- Osofsky, M.S., J.L. Kohn, E.F. Skelton, M.M. Miller, R.J. Soulem Jr and S.A. Wolf, 1992, Phys. Rev. B 45, 4916.
- Page, J.H., S.R.P. Smith and D.R. Taylor, 1984a, J. Phys. C 17, 73.
- Page, J.H., D.R. Taylor and S.R.P. Smith, 1984b, J. Phys. C 17, 51.
- Pekker, S., A. Janossy and A. Rockenbauer, 1991, Physica C 181, 11.
- Pekurovskii, V.R., 1986, Izv. Akad. Nauk. SSSR. Ser. Fiz. 50, 324.
- Pekurovskii, V.R., 1987, Fiz. Tverd. Tela 29, 1377.
- Pekurovskii, V.R., and S.I. Andronenko, 1984, Fiz. Tverd. Tela 26, 3440.

- Penney, W.G., and R. Schlapp, 1932, Phys. Rev. 41, 194.
- Petasis, D.T., N.S. Vanderven, S. Simizu and S.A. Friedberg, 1993, J. Appl. Phys. 73, 6078.
- Phillips, J.C., 1992, Phys. Rev. B 46, 8542.
- Phillips, N.E., R.A. Fisher, J.E. Gordon and S. Kim, 1989, Physica C 162–164, 1651.
- Phillips, N.E., R.A. Fisher, J.E. Gordon, S. Kim, M.K. Crawford and E.M. McCarron III, 1990, Phys. Rev. Lett. 65, 357.
- Phillips, N.E., R.A. Fisher and J.E. Gordon, 1992a, Chin. J. Phys. 30, 799.
- Phillips, N.E., R.A. Fisher and J.E. Gordon, 1992b, in: Progress in Low Temperature Physics, Vol. 13, ed. D. Brewer (Elsevier, Amsterdam) p. 267.
- Phillips, N.E., J.P. Emerson, R.A. Fisher, J.E. Gordon, B.F. Woodfield and D.A. Wright, 1994, J. Supercond. 7, 251.
- Pilawa, B., 1991, J. Phys.: Condens. Matter 3, 4293.
- Pilawa, B., G. Kess, H.G. Kahle and A. Kasten, 1988, Phys. Status Solidi (b) 145, 729.
- Piotrowski, M., B. Ptasiewicz-Bak and A. Murasik, 1979, Phys. Status Solidi (a) 55, K163.
- Pobell, F., 1982, Physica B+C 109-110, 1485.
- Podlesnyak, A., V. Kozhevnikov, A. Mirmelstein, P. Allenspach, J. Mesot, U. Staub, A. Furrer, R. Osborn, S.M. Bennington and A.D. Taylor, 1991, Physica C 175, 587.
- Pommier, J., P. Meyer, J. Ferre and I. Laursen, 1988, J. Phys. (Paris) Suppl. 49, C8-1949.
- Powell, M.J.D., and R. Orbach, 1961, Proc. Phys. Soc. 78, 753.
- Pshisukha, A.M., A.I. Zvyagin and A.S. Cherny, 1976, Fiz. Nizk. Temp. (Kiev) 2, 339.
- Purwins, H.G., and A. Leson, 1990, Adv. Phys. 39, 309.
- Quezel, G., J. Rossat-Mignod and H.Y. Lang, 1972, Solid State Commun. 10, 735.
- Rachford, F.J., and C.Y. Huang, 1971, Phys. Rev. B 3, 2121.
- Radhakrishna, P., J. Hammann and P. Pari, 1981, J. Magn. & Magn. Mater. 23, 254.
- Rappaz, M., M.M. Abraham, J.O. Ramey and L.A. Boatner, 1981, Phys. Rev. B 23, 1012.
- Redfield, A.G., 1957, IBM J. Res. Dev. 1, 19.
- Reich, D.H., T.F. Rosenbaum, G. Aeppli and H.J. Guggenheim, 1986, Phys. Rev. B 34, 4956.
- Reich, D.H., T.F. Rosenbaum and G. Aeppli, 1987, Phys. Rev. Lett. **59**, 1969.

- Reich, D.H., B. Ellman, J. Yang, T.F. Rosenbaum, G. Aeppli and D.P. Belanger, 1990, Phys. Rev. B 42, 4631.
- Reyes-Gasga, J., T. Krekels, G. Van Tendeloo, J. Van Landuyt, S. Amelinckx, W.H.M. Bruggink and M. Verweij, 1989a, Physica C 159, 831.
- Reyes-Gasga, J., T. Krekels, G. Van Tendeloo, J. Van Landuyt, W.H.M. Bruggink, M. Verweij and S. Amelinckx, 1989b, Solid State Commun. 70, 269.
- Reza, K.A., and D.R. Taylor, 1992, Phys. Rev. B 46, 11425.
- Richardson, F.S., M.P. Reid, J.J. Dallara and R.D. Smith, 1985, J. Chem. Phys. 83, 3813.
- Riedling, S., G. Brauchle, R. Lucht, K. Rohberg, H. Lohneysen, H. Claus, A. Erb and G. Müller-Vogt, 1994, Phys. Rev. B 49, 13283.
- Rimai, L., and R.W. Bierig, 1964, Phys. Rev. Lett. 12, 284.
- Riseberg, L.A., E. Cohen, W.A. Wordland and L.G. Van Uitert, 1969, Phys. Lett. A 30, 4.
- Rockenbauer, A., A. Janossy, L. Korecz and S. Pekker, 1992, J. Magn. Reson. 97, 540.
- Roessli, B., P. Fischer, M. Guillaume, J. Mesot, U. Staub, M. Zolliker, A. Furrer, E. Kaldis, J. Karpinski and E. Jilek, 1994, J. Phys.: Condens. Matter 6, 4147.
- Rohrer, H., A. Aharony and S. Fishman, 1980, J. Magn. & Magn. Mater. 15–18, 396.
- Roinel, Y., V. Bouffard, J.F. Jacquinot, C. Fermon and G. Fournier, 1985, J. Phys. (Paris) 46, 1699.
- Rosenbaum, T.F., W. Wu, B. Ellman, J. Yang, G. Aeppli and D.H. Reich, 1991, J. Appl. Phys. 70, 5946.
- Roser, M.R., and L.R. Corruccini, 1990, Phys. Rev. Lett. 65, 1064.
- Roser, M.R., J. Xu, S.J. White and L.R. Corruccini, 1992, Phys. Rev. B 45, 12337.
- Rosov, N., J.W. Lynn, H.B. Radousky, M. Bennahmias, T.J. Goodwin, P. Klavins and R.N. Shelton, 1993, Phys. Rev. B 47, 15256.
- Rossat-Mignod, J., G. Quezel, A. Berton and J. Chaussy, 1972, Phys. Status Solidi (b) 49, 147.
- Rothman, S.J., J.L. Routbort and J.E. Baker, 1989, Phys. Rev. B 40, 8852.
- Rothman, S.J., J.L. Routbort, U. Welp and J.E. Baker, 1991, Phys. Rev. B 44, 2326.
- Sakharov, V.A., 1979, Fiz. Tverd. Tela 21, 3149.
- Sakharov, V.A., 1980, Fiz. Tverd. Tela 22, 583.
- Sanchez, D., A. Junod, J.-Y. Genoud, T. Graf and J. Muller, 1992, Physica C 200, 1.
- Satoh, M., and T. Taki, 1981, Phys. Rev. B 23, 6711.

- Schlachetzki, A., and J. Eckert, 1972, Phys. Status Solidi (a) 11, 611.
- Schleger, P., W.N. Hardy and H. Casalta, 1994, Phys. Rev. B 49, 514.
- Schmidt, P.G., A. Weiss and T.P. Das, 1979, Phys. Rev. B 19, 5525.
- Schreiner, Th., R. Ahrens, T. Wolf, H. Schmidt and H. Rietschel, 1992, Physica C 204, 161.
- Schutzmann, J., S. Tajima, S. Miyamoto and S. Tanaka, 1994, Phys. Rev. Lett. 73, 174.
- Schwab, G., 1975, Phys. Status Solidi (b) 68, 359.
- Schweiss, P., W. Reihardt, M. Braden, G. Collin, G. Heger, H. Claus and A. Erb, 1994, Phys. Rev. B 49, 1387.
- Scott, P.L., and C.D. Jeffries, 1962, Phys. Rev. 127, 32.
- Semenovskaya, S., and A.G. Khachaturyan, 1992, Phys. Rev. B 46, 6511.
- Sen, H., D. Neogy and B.M. Wanklyn, 1988, J. Magn. & Magn. Mater. 73, 221.
- Sen, K.D., and P.T. Narasinahan, 1977, Phys. Rev. B 15, 95.
- Sigrist, M., and T.M. Rice, 1992, J. Phys. Soc. Jpn. 61, 4283.
- Simizu, S., and S.A. Friedberg, 1981, Physica B 108, 1099.
- Simizu, S., and S.A. Friedberg, 1982, J. Appl. Phys. 53, 1885.
- Simizu, S., and S.A. Friedberg, 1983, J. Magn. & Magn. Mater. 31-34, 1065.
- Simizu, S., G.H. Bellesis and S.A. Friedberg, 1986, J. Magn. & Magn. Mater. 54–57, 1331.
- Skanthakumar, S., H. Zhang, T.W. Clinton, I.W. Sumarlin, W.-H. Li, J.W. Lynn, Z. Fisk and S.-W. Cheong, 1990, J. Appl. Phys. 67, 4530.
- Skjeltorp, A.T., 1977, Physica B 86-88, 1295.
- Skjeltorp, A.T., 1978, J. Appl. Phys. 49, 1567.
- Skjeltorp, A.T., C.A. Catanese, H.E. Meissner and W.P. Wolf, 1973, Phys. Rev. B 7, 2062.
- Smith, M.R., Y.H. Shing, R. Chatterjee and H.A. Buckmaster, 1977, J. Magn. Reson. 26, 351.
- Sokolov, V.I., Z.A. Kazei, N.P. Kolmakova and T.V. Solov'yanova, 1991, Zh. Eksp. Teor. Phys. 99, 945 [Sov. Phys.-JETP 72, 524].
- Sokolov, V.I., Z.A. Kazei and N.P. Kolmakova, 1992a, Physica B 176, 101.
- Sokolov, V.I., M.D. Kaplan, Z.A. Kazei, A.V. Vasil'ev and A.E. Dvornikova, 1992b, J. Phys. & Chem. Solids 53, 737.
- Sterne, P.A., and L.T. Wille, 1989, Physica C 162–164, 223.

- Sternheimer, R.M., M. Blume and R.F. Peierls, 1968, Phys. Rev. **173**, 376.
- Stevens, K.W.H., 1952, Proc. Phys. Soc. A 65, 209.
- Stryjewski, E., and N. Giordano, 1977, Adv. Phys. 26, 487.
- Sun, L., Y. Wang, H. Shen and X. Cheng, 1988, Phys. Rev. B 38, 5114.
- Suzuki, H., and M. Ono, 1990, Physica B 165-166, 787.
- Suzuki, H., N. Nambudripad, B. Bleaney, A.L. Allsop, G.J. Bowden, I.A. Campbell and N.J. Stone, 1978, J. Phys. (Paris) Suppl. **39**, C6-800.
- Suzuki, H., T. Inoue and T. Ohtsuka, 1981, Physica B 107, 563.
- Suzuki, H., Yu. Masuda, M. Miyamoto, S. Sakatsume, P.J. Walker and T. Ohtsuka, 1983, J. Magn. & Magn. Mater. 31–34, 741.
- Suzuki, H., T. Ohtsuka, S. Kawarazaki, N. Kunitomi, R.M. Moon and R.M. Nicklow, 1984, Solid State Commun. 49, 1157.
- Tagirov, M.S., M.A. Teplov and L.D. Livanova, 1979, Fiz. Tverd. Tela 21, 3488.
- Tallon, J.L., and M.P. Staines, 1990, J. Appl. Phys. 68, 3998.
- Tanabe, K., S. Kubo, F. Hosseini Teherani, H. Asano and M. Suzuki, 1994, Phys. Rev. Lett. 72, 1537.
- Tang, Y.J., X.W. Cao, J.C. Ho and H.C. Ku, 1992, Phys. Rev. B 46, 1223.
- Taylor, D.R., J.P. Harrison and D.B. McColl, 1977, Physica B 86–88, 1164.
- Taylor, D.R., E. Zwartz, J.H. Page and B.E. Watts, 1986, J. Magn. & Magn. Mater. 54–57, 57.
- Teplov, M.A., 1967, Zh. Eksp. Teor. Fiz. 53, 1510 [Sov. Phys.-JETP 26, 872].
- Teplov, M.A., 1968, Zh. Eksp. Teor. Fiz. 55, 2145 [Sov. Phys.-JETP 28, 1136].
- Teplov, M.A., 1977, in: Crystal Field Effects in Metals and Alloys, ed A. Furrer (Plenum Press, N.Y.) p. 318.
- Teplov, M.A., O.N. Bakharev, A.V. Dooglav, A.V. Egorov, M.V. Eremin, M.S. Tagirov, A.G. Volodin and R.Sh. Zhdanov, 1991, Physica C 185–189, 1107.
- Teplov, M.A., O.N. Bakharev, A.V. Dooglav, A.V. Egorov, E.V. Krjukov, O.V. Marvin, V.V. Naletov, A.G. Volodin and D. Wagener, 1994, Physica C 235–240, 265.
- Teplov, M.A., O.N. Bakharev, H.B. Brom, A.V. Dooglav, A.V. Egorov, E.V. Krjukov, O.V. Marvin, I.R. Mukhamedshin, V.V. Naletov, A.G. Volodin,

D. Wagener and J. Witteveen, 1995, J. Supercond. 8, 413.

- Thalmeier, P., and P. Fulde, 1978, Z. Phys. B 29, 299.
- Thoma, R.E., G.D. Brunton, R.A. Penneman and T.K. Keenan, 1970, Inorg. Chem. 9, 1096.
- Tolentino, H., F. Baudelet, A. Fontaine, T. Gourieux, G. Krill, J.Y. Henry and J. Rossat-Mignod, 1992, Physica C 191, 115.
- Triplett, B.B., and R.M. White, 1973, Phys. Rev. B 7, 4938.
- Tse, D., and S.R. Hartmann, 1968, Phys. Rev. Lett. 21, 511.
- Vaisfel'd, M.P., 1972, Fiz. Tverd. Tela 14, 737 [Sov. Phys.-Solid State 14, 628].
- Vaknin, D., J.L. Zarestky, D.C. Johnston, J.E. Schirber and Z. Fisk, 1994, Phys. Rev. B 49, 9057.
- Van Vleck, J.H., 1932, The Theory of Electric and Magnetic Susceptibilities (Oxford University Press).
- Vasil'ev, A.V., A.E. Dvornikova, Z.A. Kazei, B.V. Mill, M.D. Kaplan and V.I. Sokolov, 1989, Zh. Eksp. Teor. Fiz. Pis'ma Red. 50, 90.
- Veal, B.W., A.P. Paulikas, H. You, H. Shi, Y. Fang and J.W. Downey, 1990, Phys. Rev. B 42, 6305.
- Vedrine, A., J.P. Besse, G. Baud and M. Capestan, 1970, Rev. Chim. Miner. 7, 593.
- Veenendaal, E.J., and H.B. Brom, 1982, Physica B+C 113, 118.
- Veenendaal, E.J., H.B. Brom and W.J. Huiskamp, 1983, Physica B 121, 1.
- Vekhter, B.G., and M.D. Kaplan, 1984, Zh. Eksp. Teor. Fiz. 87, 1774.
- Vekhter, B.G., Z.A. Kazei, M.D. Kaplan and V.I. Sokolov, 1986, Zh. Eksp. Teor. Fiz. Pis'ma Red. 43, 287 [JETP Lett. 43, 369].
- Vekhter, B.G., Z.A. Kazei, M.D. Kaplan, B.V. Mill and V.I. Sokolov, 1988, Fiz. Tverd. Tela 30, 1021 [Sov. Phys.-Solid State 30, 592].
- Vekhter, B.G., Z.A. Kazei, M.D. Kaplan and Yu.F. Popov, 1991, Zh. Eksp. Teor. Fiz. Pis'ma Red. 54, 575.
- Vinokurov, A.V., B.Z. Malkin, A.I. Pominov and A.L. Stolov, 1986, Fiz. Tverd. Tela 28, 381 [Sov. Phys.-Solid State 28, 211].
- Vinokurov, A.V., S.L. Korableva, B.Z. Malkin, A.I. Pominov and A.L. Stolov, 1988a, Fiz. Tverd. Tela 30, 801 [Sov. Phys.-Solid State 30, 459].
- Vinokurov, A.V., A.M. Korovkin, B.Z. Malkin, V.R. Pekurovskii, A.I. Pominov and A.L. Stolov, 1988b, Fiz. Tverd. Tela 30, 2415. [Sov. Phys.-Solid State 30, 1392].

- Vinokurov, A.V., B.Z. Malkin, A.I. Pominov and A.L. Stolov, 1988c, Fiz. Tverd. Tela 30, 3426 [Sov. Phys.-Solid State 30, 1966].
- Vishwamittar, X., and S.P. Puri, 1974, J. Phys. C 7, 1337.
- Viswanathan, C.R., and E.Y. Wong, 1968, J. Chem. Phys. 49, 966.
- Volodin, A.G., A.V. Egorov, M.S. Tagirov, M.A. Teplov, G. Feller, H. Schwabe and M. Schtaudte, 1986, Zh. Eksp. Teor. Fiz. Pis'ma Red. 43, 295.
- Voronkova, V.I., V.K. Yanovskii, V.N. Molchanov, N.I. Sorokina and V.I. Simonov, 1990, Zh. Eksp. Teor. Fiz. Pis'ma Red. 52, 854.
- Wachter, P., B. Bucher and R. Pittini, 1994, Phys. Rev. B 49, 13164.
- Waller, I., 1932, Z. Phys. 79, 370.
- Wangsness, R.K., and F. Bloch, 1953, Phys. Rev. 89, 728.
- Wanklyn, B.M., 1973, J. Mater. Sci. 8, 649.
- Welp, U., M. Grimsditch, S. Fleshler, W. Nessler, J.W. Downey, G.W. Crabtree and J. Guimpel, 1992, Phys. Rev. Lett. 69, 2130.
- Wheatley, J.C., 1975, Rev. Mod. Phys. 47, 415.
- Will, G., and W. Schäfer, 1971, J. Phys. C 4, 811.
- Will, G., W. Schäfer, W. Scharenberg and H. Gobel, 1971, Z. Angew. Phys. 32, 122.
- Wolf, W.P., and C.H.A. Huan, 1988, Phys. Rev. B 37, 2023.
- Wolf, W.P., M.J.M. Leask, B.W. Mangum and A.F.G. Wyatt, 1961, J. Phys. Soc. (Jpn) 17, Suppl. B1, 487.
- Wolfe, J.P., 1973, Phys. Rev. Lett. 31, 907.
- Wolfe, J.P., and C.D. Jeffries, 1971, Phys. Rev. B 4, 731.
- Wolfsberg, M., and L. Helmholz, 1952, J. Chem. Phys. 20, 837.
- Wortmann, G., and I. Felner, 1990, Solid State Commun. 75, 981.
- Wright, J.C., H.W. Moos, J.H. Colwell, B.W. Mangum and D.D. Thornton, 1971, Phys. Rev. B 3, 843.
- Wu, W., D. Bitko, T.F. Rosenbaum and G. Aeppli, 1993, Phys. Rev. Lett. 71, 1919.
- Xie, X.M., T.G. Chen and Z.L. Wu, 1989, Phys. Rev. B 40, 4549.
- Xu, H.-J., B. Bergersen and Z. Racz, 1992, J. Phys.: Condens. Matter 4, 2035.
- Xu, J., and L.R. Corruccini, 1987, Jpn. J. Appl. Phys. 26(Suppl. 26-3), 813.
- Xu, J., M.R. Roser and L.R. Corruccini, 1990, J. Low Temp. Phys. 78, 13.

- Yang, K.N., J.M. Ferreira, B.W. Lee, M.B. Maple, W.-H. Li, J.W. Lynn and R.W. Erwin, 1989, Phys. Rev. B 40, 10963.
- Yang, S., H. Claus, B.W. Veal, R. Wheeler, A.P. Paulikas and J.W. Downey, 1992, Physica C 193, 243.
- Young, A.P., 1975, J. Phys. C 8, 3158.
- Youngblood, R.W., G. Aeppli, J.D. Axe and J.A. Griffin, 1982, Phys. Rev. Lett. 49, 1724.
- Zeiske, T., R. Sonntag, D. Hohlwein, N.H. Andersen and T. Wolf, 1991, Nature 353, 542.
- Zhang, H., J.W. Lynn and D.E. Morris, 1992a, J. Magn. & Magn. Mater. 104–107, Part II, 821.

- Zhang, H., J.W. Lynn and D.E. Morris, 1992b, Phys. Rev. B 45, 10022.
- Zhang, H., Y.Y. Wang, V.P. Dravid, B. Dabrowski and K. Zhang, 1993, Physica C 207, 167.
- Zhdanov, R.Sh., F.L. Aukhadeev, A.B. Liberman, N.I. Silkin, M.A. Teplov, Sh.J. Yagudin and M.Sh. Yagfarov, 1983, Fiz. Tverd. Tela 25, 929.
- Zvyagin, A.I., T.S. Stetsenko, V.G. Yurko and R.A. Vaishnoras, 1973, Zh. Eksp. Teor. Fiz. Pis'ma Red. 17, 190 [JETP Lett. 17, 135].

Handbook on the Physics and Chemistry of Rare Earths Vol. 22 edited by K.A. Gschneidner, Jr. and L. Eyring © 1996 Elsevier Science B.V. All rights reserved

Chapter 151

COHERENT EMISSION IN RARE-EARTH MATERIALS

F. Auzel

France Telecom, CNET PAB, Laboratoire de Bagneux, B.P. 107, 92225 Bagneux, France

Contents

	List of symbols	508
1.	Introduction	510
	1.1. History	510
	1.2. Scope of the chapter	511
2.	Basic processes involved in coherent sources	511
	2.1. Superradiance and superfluorescence	512
	2.1.1. Induced and spontaneous	
	transitions in the two-level atom	512
	2.1.1.1. The Rabi equation in the	
	fully quantized approach	516
	2.1.1.2. Synchronous exchange	
	between field and atom	516
	2.1.1.3. The pseudo-spin Bloch	
	vector of the two-level	
	system	517
	2.1.1.4. Spontaneous emission	
	and the Weisskopf-	
	Wigner damping	519
	2.1.2. Merging of coherent emission	500
	and spontaneous decay	522
	2.1.2.1. Damping of Rabi	
	oscillation by	500
	spontaneous decay	522
	2.1.2.2. The link between the	522
	various relaxation times	525
	2.1.3. Field-coupled cooperative multi-	524
	2 1 3 1 Superradiance	525
	2.1.3.1. Superfluorescence (SF)	527
	2.1.3.2. Superhabits conce (Sr)	527
	2.1.3.2.1. The conditions for	140
	SF	530
	2.1.4 Experimental results	
	for superradiance and	

			superfluorescence in rare-earth	
			(R) ion systems	531
			2.1.4.1. Superradiance (SR) and	
			R ions	531
			2.1.4.2. Superfluorescence (SF)	
			in the solid state and in	
			R ions	531
			2.1.4.3. SF applications	536
	2.2.	Ampli	fication of spontaneous emission	
		by stir	nulated emission and the laser	
		effect		536
		2.2.1.	Amplified spontaneous emission	
			(ASE)	536
		2.2.2.	Examples of ASE in R-doped	
			media in comparison with SF	537
			2.2.2.1. ASE in doped fibers	537
			2.2.2.2. ASE in R-doped powders	538
		2.2.3.	The laser effect	540
3.	Basi	с ргос	esses in R-doped materials for	
	laser	s	·····	542
	3.1.	Radiat	ive properties	542
		3.1.1.	Oscillator strengths and	
			hypersensitive transitions	542
		3.1.2.	Branching ratios and quantum	
			efficiencies	543
	3.2.	Non-r	adjustive transitions and vibronics	544
	3.3.	Energy	v transfers and up-conversion	549
		3.3.1.	Energy transfer with the activator	
			in its ground state	549
		3.3.2.	Up-conversion processes	555
			3.3.2.1. Up-conversion in single-	
			ion-level description	
			(APTE) and in pair-level	
			description (cooperative	
			effects)	558

	_		3.3.2.2. ESA and the APTE effect 3.3.2.3. Photon avalanche effect	560 561
4.	Engineering approach to R materials for			
	lase	rs		564
	4.1.	Mater	als for CW lasers	262
		4.1.1.	Powdered samples luminescence	
			as an approach to Figure of Merit	
			(global optimization of M)	565
		4.1.2.	Self-quenching and crystal field	
			strength (optimization of the	
			product τN_0)	567
		4.1.3.	Optimization of line strength and	
		-	cross-section	574
	4.2.	The h	igh-power laser case	577
		4.2.1.	Thermal properties for high	
			average power lasers	577
		4.2.2.	Optical properties for high peak	
			power and high power density	
_			lasers	579
5.	Rece	ent adv	ances in R lasers	580
	5.1.	R-dop	ed fibers for amplifiers and lasers	580
		5.1.1.	The peculiar case of fibers for	
			3-level amplifiers and lasers	580
			5.1.1.1. Fiber intrinsic properties	582
			5.1.1.1.1. The single-mode	
			condition	582
			5.1.1.1.2. Transmission	
			properties	582
			5.1.1.2. Spectroscopic properties	
			of fibers: comparison	
			with bulk samples	583
			5.1.1.2.1. Absorption	583
			5.1.1.2.2. Emission	583

5.1.1.2.3. Radiative energy	
transfer	584
5.1.1.3. Adequacy of fibers for	
laser diode pumping	584
5.1.2. Basic comparison between silica	
and fluoride fibers	584
5.1.3. Examples of doped fiber	
amplifiers and lasers	586
5.1.3.1. Er ³⁺ in silica glass at	
1.55 µm	587
5.1.3.2. Heavy fluoride glasses	
doped with Er ³⁺ , Pr ³⁺ ,	
Tm^{3+}	588
5.2. Up-conversion lasers	590
5.2.1. Anti-Stokes lasers in crystals	591
5.2.2. Anti-Stokes lasers in fluoride	
glass fibers	591
5.2.3. Up-conversion laser with	
multiphonon-assisted pumping	
scheme and photon avalanche	592
5.3. R-doped semiconductors and single-	
mode semiconductor lasers by coupling	
to R-doped insulators	594
5.3.1. Semiconducting III-V	
compounds and elemental	
semiconductors doped with Er ³⁺	594
5.3.2. Low-field electroluminescence	595
5.3.3. Er ³⁺ and GaInAsP lasers for	
single-mode emission at $1.5\mu m$	597
Concluding remarks and hints for future	
trends	599
Acknowledgements	
References	600

List of symbols

a	fiber core diameter	C_S^N	combination number of N objects
a+, a	photon creation (a^{+}) and		among S
	annihilation (a) operators	C, C_{ss}	energy transfer constants
$A, W_{\rm R}$	spontaneous emission probability	d	electric dipole operator
В	induced emission Einstein coefficient	D	energy transfer diffusion constant
B_q^k	crystal field parameter	$ e\rangle$	two-level atom excited state wave
с	speed of light in vacuum		function
$C_{k}(t)$	time-dependent coefficient of wave	E_{1}, E_{2}	energies of states 1, 2
	function	ΔE	field induced energy shift
Ċ _k	first derivative of C_k with respect to	e_2, e_1	energies of level 2 and 1 barycenters
	time	f_{ii}, A_{ii}	oscillator strength for electron
C_q^k	q-component of spherical tensor operator of rank k		transition $i \rightarrow j$ and corresponding spontaneous probability

6.

Fresnel number	R _{min}
two-level atom ground-state wave	R_0
function	R _N
normalized spectrum line shape	S, L
electric dipole matrix element (g) and	S
conjugate (g*)	$S^*, S^0, A^*,$
level degeneracy	A^0
	S_0
Plank constant $(\hbar = h/2\pi)$	
Hamiltonian operator	S
interaction Hamiltonian between	$S(=\tau_{\rm R}/\tau_{\rm L})$
sensitizer and activator	Т
spectral overlap integral	T
fluorescence, absorbed and incident	T_{1}, T_{2}
intensities	1. 2
total orbital momentum quantum	T'_{2}, T^{*}_{2}
numbers	
Boltzmann's constant	T_{λ}
thermal conductivity; constant for	U^{λ}
nonlinear parameter	
sample length	V(t)
Neperian log	W_i, W_{ii}
mass and charge of the electron	W ₁₂
superradiance macro-dipole	
laser material Figure of Merit	W _{NR}
photon state number	$Y_{kq}(\theta, \varphi)$
Second-order nonlinear index of	α.

	nonlinear parameter
L	sample length
log _n	Neperian log
m, e	mass and charge of the electron
$\langle M \rangle$	superradiance macro-dipole
М	laser material Figure of Merit
n	photon state number
<i>n</i> ₂	Second-order nonlinear index of refraction
<i>n</i> _D , <i>n</i>	refractive index at considered transition pulsation ω_{ii}
n	average phonon state number
Ν	multiphonon order for multiphonon transition
N ₀	ground-state population or active ion chemical concentration
N_{1}, N_{2}	population density of states 1, 2
$N_{\rm A}, N_{\rm S}$	activator and sensitizer concentrations
N_V	Auzel's scalar crystal field parameter
NA	fiber numerical aperture
Р	radiated power per unit volume
$p_t^{(N)}, p_t,$	multiphonon probabilities
$p(N), p_{\ell}$	
Q	cavity quality factor
R	rare-earth entity
R	mirror reflection coefficient

F

 $|g\rangle$

g(v)

g, g*

Η

 $H_{\rm SA}$

 I, S_{SA}

J, J'

k K

 $I_{\rm f}, I_{\rm a}, I_{\rm i}$

 $g_1, g_2, g_8,$ g_A ħ, h

R _{min}	minimum sensitizer-activator distance
R_0	Dexter's critical distance
R _N	Huang–Rhys function
S, L	total spin and orbit quantum numbers
S	sample geometrical cross section
S*, S ⁰ , A*, A ⁰	sensitizers and activators in excited* and ground ⁰ states
S ₀	Huang-Rhys electron-phonon coupling parameter
S	pseudo-spin Bloch vector
$S(=\tau_{\rm R}/\tau_{\rm L})$	cavity output coupling
T	absolute temperature
Т	vector of Bloch relaxation times
T_{1}, T_{2}	Bloch longitudinal and transverse relaxation times
<i>T</i> ' ₂ , <i>T</i> [*] ₂	homogeneous and inhomogeneous contribution to T_2
T_{λ}	Judd's parameter of order λ
U^{λ}	unit irreducible tensorial operators of rank λ (= 2, 4, 6)
V(t)	time-dependent perturbation
W_i, W_{ij}	probabilities
W ₁₂	transition probability per unit time between states 1 and 2
W _{NR}	non-radiative transition probability
$Y_{kq}(\theta, \varphi)$	spherical harmonic
α	absorption coefficient
α	multiphonon exponential parameter for non-radiative transition
$\alpha_{\rm SA}$	spectral overlap integral
β	multiphonon exponential parameter for transfers
β_{ii}	branching ratio for transition $i \rightarrow j$
Г	homogeneous natural width
γ	laser cavity losses
γ	cubic coefficient for non-harmonicity
γ	nonlinear coefficient
δ	delta function
δ	delta function unit vector
ε_0	dielectric constant
ε _{kλ}	polarization vector for wavevector k at pulsation ω_k
η	transition quantum efficiency
η_i, τ_i	quantum efficiency and measured lifetime of level <i>i</i>

F. AUZEL

$egin{array}{l} \Theta \ \lambda_0 \ \Delta \overline{oldsymbol{ u}} \end{array}$	Debye temperature wavelength corresponding to ω_0 effective linewidth of considered transition	$\tau_{\rm SR}$ ϕ_k $\phi_{\rm p}, \phi_{\rm th}$	superradiance lifetime time-independent wave function pumping flux, threshold pumping flux local field correction
ρ ρ $\sigma^{+,-}$ σ_{2}	population inversion density density of final states raising (+) and lowering (-) operators laser cross-section	χ^{ω}_{ij} Ψ, Ψ' $\Psi(r, t)$	linear susceptibilities at pulsation ω complementary quantum numbers time- and space-dependent wave function
$\sigma_{\rm p}$ $\tau_{\rm 0}$ $\tau_{\rm c}, \ell_{\rm c}$	pump transition cross-section radiative lifetime ($\tau_0 = T_1$) Arrechi–Courtens cooperation time and distance	$egin{array}{c} \Omega & & \ \Omega_0 & & \ \Omega_\lambda & & \ \Omega & & \ \end{array}$	Rabi pulsation Rabi pulsation for resonant field reduced Judd's parameter of order λ
τ_{d} τ_{E} τ_{R}, τ_{L} τ_{S}, τ_{D} τ_{SF}	superfluorescent time delay photon escape time from sample contributions of mirror and material losses to photon escape time sensitizer and diffusion lifetime superfluorescence lifetime	$\omega_0 \\ \omega_2, \ldots, \\ \omega_{n-1} \\ \omega_k \\ \omega_m$	atom resonant pulsation probabilities pulsation corresponding to energy E_k maximum or effective phonon pulsation

1. Introduction

1.1. History

Very shortly after the first demonstration of the laser effect in Al_2O_3 :Cr³⁺ by Maiman (1960), the specific abilities of rare-earth (R) ions in laser emission were demonstrated by Johnson and Nassau (1961) in WO₄Ca:Nd³⁺; Snitzer (1961) in a Nd³⁺ doped silica glass fiber; Kaiser et al. (1961) in CaF₂:Sm²⁺; and Sorokin et al. (1962) in SrF₂:Sm²⁺; even R in liquids were considered (Lempicki and Samelson 1963). At the same time, the CNET Group (1963) proposed the use of Nd³⁺-doped phosphate fibers in order to avoid the problem of the glass optical quality, encountered in the first Nd³⁺ laser phosphate glass in bulk (Deutschbein et al. 1964). Such Nd³⁺ phosphate glass allowed the first CW laser functioning in a glass (Deutschbein and Pautrat 1968).

Within a few years these very first results were followed by laser effects in other R ions such as Pr^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , Dy^{2+} . In particular Er^{3+} laser emission at 1.5 μ m was obtained in silica glass (Snitzer and Woodcock 1965), and studied in phosphate, beryllium fluoride, fluorophosphate glasses (Auzel 1966a, 1968). All these pioneer results have already been reviewed in several books (for instance, Di Bartolo 1968, Roess 1969, Weber 1979 in volume 4 of this Handbook; Kaminskii 1981, Reisfeld and Jørgensen 1977).

Among the R ions, Nd³⁺ played a special role linked with the well-behaved positions of its first four excited states: they allow a "four-level" laser scheme with good quantum efficiency even in materials with relatively high phonon energy such as oxides, or even liquids.

510

However, since 1986, new laser schemes and applications are emerging, which push Er^{3+} to the forefront: between 1987 and 1990, 600 papers have appeared dealing only with the amplification properties of Er^{3+} (Sunak 1991). Also the replacement of broad-spectrum pumping sources (black body types) by monochromatic ones, such as a primary laser, has revived many of the older schemes which were known but not yet applied.

Also, a better understanding since the mid seventies, of the basic processes, such as multiphonon interaction and energy transfers linked with laser materials, has brought on an engineering type approach for new materials research (Auzel 1987). Finally, the enormous development of R-doped fibers has opened the door to many new laser and amplifier schemes (see Digonnet 1993, Desurvire 1994 and Becker et al. 1996 for recent reviews).

For all these reasons, a critical review of some recent key results in the light of the basic processes involved, is certainly timely and such is the scope of the present review.

1.2. Scope of the chapter

In previous reviews, R-doped materials were considered essentially in relation with the laser effect itself. Here we would like to introduce the coherent emission from rare earths in a broader sense than usual, and so present the background of the different types of emission: superradiance, superfluorescence, and amplification of spontaneous emission by stimulated emission, such effects being considered beside the laser effect. Besides this, we shall expose the foundations of up-conversion by energy transfers (APTE effect) (Auzel 1966b, 1973) in comparison with cooperative up-conversion (Ovsyankin and Feofilov 1966, Nakazawa and Shionoya 1970). Up-conversion by the avalanche effect (Chivian et al. 1979) shall also be presented, because up-conversion pumping of a laser is the recent trend in this field which has been recently reviewed by Joubert et al. (1993). Then we shall present an engineering approach for the research of laser materials. Meanwhile we shall deal with some recent evidence for coherent spontaneous emission in R-doped materials and we shall review some recent advances in R lasers and amplifiers.

In this presentation, the purpose is not to be exhaustive but rather to dwell mainly on concepts, turning points in the recent advances, and on what we believe to be important key results, all this in a coherent self-consistent approach.

2. Basic processes involved in coherent sources

Besides the well-known relaxation paths for an excited state (fluorescence emissions, nonradiative transitions, energy transfers), there is a number of other processes which may arise when excited states are highly populated, namely: coherent emission either of the stimulated or of the spontaneous type (superfluorescence), excited state absorption with or without energy transfers.

In this section we shall present some unusual behaviors starting from the more classical ones which are predominant at lower excitation levels. We shall see how spontaneous emission merges into a stimulated one or into coherent spontaneous emission. In sect. 2.1 we shall try to distinguish between superradiance (SR) and superfluorescence (SF), and in sect. 2.2 to distinguish these from amplified spontaneous photons by stimulated emission (ASE). The difference with the laser effect is discussed in sect. 2.2.3.

2.1. Superradiance and superfluorescence

With the advent of laser excitation, bringing its high power density together with its coherence, a number of spectroscopic processes otherwise neglected have to be considered. In this section we shall deal first with the basic process of stimulated transitions and their intermingling with spontaneous emission right from their common origin: the coupling of the atom state with the quantized electromagnetic field. We shall see how the spontaneous emission appears as a damping term in the Rabi solution of the problem, explaining how some phase memory of the states' wave functions may be kept during emission, giving rise to coherent spectroscopic properties, among them superfluorescence. In fact there are three types of coherent emissions connected with spontaneous emission, which differ from laser emission by the common feature that they do not require a closed optical cavity: Dieke superradiance (SR) (Dieke 1954), superfluorescence (SF) (Bonifacio and Lugiato 1975), and spontaneous emission amplified by stimulated emission (ASE) (Waite 1964). Though these effects have sometimes been confused with each other, conditions to distinguish between them have been specified by Bonifacio and Lugiato (1975). We shall see how SR is caused by an ensemble of coherently prepared two states atoms emitting spontaneously in cooperation within a volume $<\lambda^3$. As for SF, atoms being prepared incoherently in their excited state, emit a cooperative spontaneous emission by a self-organization stemming from their common emitted field. Though sometimes called superradiance, ASE is just what would happen in a long laser medium without a mirror. Such a situation is quite like the one of a mirror multifolded laser cavity; propagation then plays an important role which is not necessary for pure SR and SF cases.

Typical of these coherent spontaneous emissions is the reduced fluorescent lifetime which can become much shorter than the non-radiative decay. Then the radiative process may even overtake the non-radiative one.

2.1.1. Induced and spontaneous transitions in the two-level atom

In the absence of a strong excitation field, which is the case with classical spectroscopy before the use of lasers, an induced transition between two levels would be described by the well-known Golden Fermi Rule based on first-order perturbation theory

$$W_{12} = \frac{2\pi}{\hbar} |\langle 2 | V(t) | 1 \rangle|^2 \,\delta(E_2 - E_1 - E), \tag{1}$$

where W_{12} is the probability per unit time for a transition from state 1 to 2 under a timedependent perturbation V(t). However, applicability of such a relation requires a number of conditions. In particular, the ground-state population in level 1 must stay about constant under the interaction, that is, strong pumping is avoided; also $W_{12}t$ should be $\ll 1$. This means

$$t\ll \frac{1}{W_{12}},$$

a short time interaction adapted to the transition probability.

Since in the following we are interested in large changes in level population, we have to consider the full time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(r,t)\right\rangle = H\left|\Psi(r,t)\right\rangle,\tag{2}$$

where $H = H_0 + V(t)$ is the time-dependent Hamiltonian, with H_0 the time-independent part and V(t) the time-dependent one.

Since we are interested mainly in the roots of spontaneous emission, we shall quantize the electromagnetic field because we know that the semi-classical description where the atom is quantized and the field is classical, does not provide any spontaneous emission: it is introduced phenomenologically by a detailed balance of the population of the twostates atom and comparison with Planck's law. This procedure introduced by Einstein gave the well-known relationship between induced absorption (or emission), and spontaneous emission probabilities, the B_{12} , B_{21} and A_{21} coefficients, respectively, but cannot produce the coherent aspect and its link with spontaneous emission.

Solutions to eq. (2) are obtained by projecting the time-dependent wavefunctions on the time-independent one

$$\Psi(r,t)\sum_{k}C_{k}(t)\left|\phi_{k}(r)\right\rangle e^{-i\omega_{k}t},$$
(3)

with $\omega_k = E_k/\hbar$ and eq. (2) becomes

$$i\hbar \dot{C}_{l}(t) = \sum_{k} C_{k}(t) \langle \phi_{l}(r) | V(t) | \phi_{k}(r) \rangle e^{i\omega_{lk}t}, \qquad (4)$$

with $\omega_{lk} = \omega_l - \omega_k$.

For our two-state systems, eq. (4) becomes

$$i\hbar \dot{C}_{1}(t) = C_{2}(t) \langle \phi_{1}(r) | V(t) | \phi_{2}(r) \rangle e^{i\omega_{12}t},$$
(5)

$$i\hbar \dot{C}_2(t) = C_1(t) \langle \phi_2(r) | V(t) | \phi_1(r) \rangle e^{i\omega_{21}t}.$$
(6)

 $C_1^2(t)$ and $C_2^2(t)$ describe the probabilities for the system to be in state ϕ_1 or ϕ_2 , with the normalization

$$\left|C_{1}^{2}(t)\right| + \left|C_{2}^{2}(t)\right| = 1.$$
(7)

For the steady-state Hamiltonian (H_A) of the atom one has

$$H_{\rm A} |e\rangle = \frac{1}{2}\hbar\omega_0 |e\rangle, \qquad H_{\rm A} |g\rangle = \frac{1}{2}\hbar\omega_0 |g\rangle, \qquad (8.9)$$

with the energy origin taken half-way between the ground state $|g\rangle$ and the excited state $|e\rangle$ of the atom. Multiplying eq. (8) by $\langle e|$ and eq. (9) by $\langle g|$ and subtracting one obtains

$$H_{\rm A} = \frac{1}{2}\hbar\omega_0\sigma_{\rm z},\tag{10}$$

where

$$\sigma_{z} = \sigma^{+}\sigma^{-} - \sigma^{-}\sigma^{+} = |e\rangle \langle e| - |g\rangle \langle g|,$$

 σ^+ and σ^- being "raising" and "lowering" operators: the names of σ^+ and σ^- come from the following relationships:

$$\sigma^+ \ket{g} = \ket{e}; \qquad \sigma^- \ket{e} = \ket{g}.$$

Now the field part of the steady state Hamiltonian is written in terms of photon creation (a^+) and photon annihilation (a) operators

$$H_{\rm F} = \hbar \omega a^{\dagger} a; \tag{11}$$

then the steady state Hamiltonian is

$$H_0 = \frac{1}{2}\hbar\omega_0\sigma_z + \hbar\omega a^+ a,\tag{12}$$

with the following initial and final states for emission:

$$|1\rangle = |e,n\rangle \rightarrow |2\rangle = |g,n+1\rangle, \tag{13}$$

and equivalently for absorption:

$$|1\rangle = |g,n\rangle \rightarrow |2\rangle = |e,n-1\rangle; \tag{14}$$

when the atom gains energy the number of photon states (n) is reduced by one unit, and reciprocally, when the atom loses energy, (n) is increased by one.

The energy difference between the two states of the complete system is

$$\hbar\omega_{21} = \hbar(\omega_0 - \omega),\tag{15}$$

where ω_0 is the atom resonance pulsation, and ω the electromagnetic field pulsation.

514

The time-dependent interaction V(t) promoting the transition is assumed to be due only to the establishment of the coupling of the electric field E(r) with the electric dipole operator (d) of the atom

$$V(t) = H_{\rm AF} = -d \cdot E(r), \tag{16}$$

using the quantized form of the field

$$H_{\rm AF} = -i \sum_{k,\lambda} \sqrt{\frac{\hbar \omega_k}{2\varepsilon_0 V}} d \cdot \varepsilon_{k\lambda} (a_{k\lambda} \cdot e^{ikr} - a_{k\lambda}^+ \cdot e^{-ikr}), \qquad (17)$$

where k is the wave vector for pulsation ω_k , $\varepsilon_{k\lambda}$ is the polarization vector, and V is the volume of the cavity containing the electromagnetic field. Equation (16) can be written as

$$H_{\rm AF} = \hbar \left(g \sigma^+ - g^* \sigma^- \right) \left(a - a^+ \right), \tag{18}$$

with

$$\hbar g = -i \sqrt{\frac{\hbar \omega}{2\varepsilon_0 V}} \langle e | d \cdot \varepsilon | g \rangle, \qquad \hbar g^* = -i \sqrt{\frac{\hbar \omega}{2\varepsilon_0 V}} \langle e | d \cdot \varepsilon | g \rangle, \qquad (19,20)$$

Equations (19) and (20) are recognized to be the electric dipole matrix elements of the atom and characterize the strength of the possible atomic transitions.

In the product (18), the terms $-g^*\sigma^-a$ and $-g^*\sigma^+a^+$ are assumed to be zero because one cannot "lower" the atom and annihilate a photon nor "raise" the atom and create a photon. Then:

$$H_{\rm AF} = \hbar (ga\sigma^+ + g^*a^+\sigma^-). \tag{21}$$

The matrix elements in eqs. (5) and (6) for the transition between states given in eqs. (13) and (14) now become

$$\langle \phi_1(r) | V(t) | \phi_2(r) \rangle \equiv \langle 1 | H_{\rm AF} | 2 \rangle, \qquad \langle \phi_2(r) | V(t) | \phi_1(r) \rangle \equiv \langle 2 | H_{\rm AF} | 1 \rangle,$$

or, for emission,

$$\langle 2 | H_{\rm AF} | 1 \rangle = \hbar g^* \langle g | g \rangle \langle n+1 | a^+ | n \rangle.$$

Since

$$a^{+}\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle,\tag{22}$$

one has

$$\langle 2 | H_{\rm AF} | 1 \rangle = \hbar g^* \sqrt{n+1}. \tag{23}$$

For absorption this would be

$$\langle 1 | H_{\rm AF} | 2 \rangle = \hbar g \sqrt{n}. \tag{24}$$

since

$$a \left| n \right\rangle = \sqrt{n} \left| n - 1 \right\rangle, \tag{25}$$

Comparison of eqs. (23) and (25) shows that the main difference between emission and absorption is that emission may exist even in the absence of an external field (n=0), which

is the spontaneous emission we are interested in. The case $n \neq 0$ allows the existence of both induced emission and absorption.

2.1.1.1. The Rabi equation in the fully quantized approach. In the following, we derive the coherent part which can exist even in spontaneous emission. We insert matrix elements (26) and (29) into the time-dependent Schrödinger equation for our two-level system, eqs. (5) and (6):

$$i\hbar\dot{C}_1(t) = C_2(t)\hbar g\sqrt{n} e^{i\omega_{12}t},$$
 (26)

$$i\hbar\dot{C}_2(t) = C_1(t)\hbar g^*\sqrt{n+1} e^{i\omega_{12}t},$$
(27)

and we shall specify the following initial conditions

$$C_1(0) = 1;$$
 $C_2(0) = 0;$ $C_1(t) \neq 1,$ (28)

that is, the system starts from a fully populated state and is allowed to change its state drastically.

The solution to eqs. (26) and (27) is found to be

$$C_2(t) = \frac{2\mathrm{i}|g|}{\Omega} \sqrt{n+1} \mathrm{e}^{(\mathrm{i}/2)(\omega 0 - \omega)t} \mathrm{sin} \frac{1}{2} \Omega t, \tag{29}$$

where

$$\Omega = \sqrt{\omega_{12}^2 + 4g^2 n^{1/2} (n+1)^{1/2}},\tag{30}$$

which is the Rabi equation for $C_2(t)$ in the field quantized case. Ω is called the Rabi frequency or the nutation frequency.

Equation (30) shows that Ω differs only by the term $\sqrt{n(n + 1)}$ instead of *n* from the one generally considered (Weissbluth 1989). In a strong external field n > 1 and eq. (29) is the general result.

2.1.1.2. Synchronous exchange between field and atom. We shall consider first the case of a strong external field in resonance with the atom $(n > 1 \text{ and } \omega_{12} = 0)$. Then

$$\Omega = \Omega_0 = 2g\sqrt{n},\tag{31}$$

and eq. (29) becomes

$$C_2(t) = \mathbf{i} \sin \frac{1}{2} \Omega_0 t. \tag{32}$$

The probability of finding the system in state 2 is

$$|C_2(t)|^2 = \sin^2 \frac{\Omega_0 t}{2},$$
(33)

and this is also the probability for the transition $1 \rightarrow 2$.



Fig. 1. $|C_2|^2$ for a resonant ($\omega_{12}=0$) and for an off-resonant case ($\omega_{12}=0.5 \Omega_0$).

Similarly, from eq. (7) we have:

$$|C_1(t)|^2 = 1 - \sin^2 \frac{1}{2} \Omega_0 t = \cos^2 \frac{1}{2} \Omega_0 t, \tag{34}$$

which is the probability for a transition $2 \rightarrow 1$. Figure 1 shows $|C_2(t)|^2$ for $\omega_{12} = 0$ and $\omega_{12} = 0.5\Omega_0$.

Let us now calculate the dipole moment during the process: $\langle \Psi(t) | e \cdot d | \Psi(t) \rangle$ with

$$\Psi(t) = i \sin \frac{1}{2} \Omega_0 t \phi_2 + \cos \frac{1}{2} \Omega_0 t \phi_1, \tag{35}$$

showing that the system is in a mixed state except at extrema $(t = 0; t = \pi/\Omega_0; t = 2\pi/\Omega_0; ...)$. Because H_{AF} is the dipolar interaction, assuming g to be real for simplicity, one has from eqs. (34), (35) and (3):

$$\langle e \cdot d \rangle = \frac{1}{4} \hbar \Omega_0 \sin \omega_0 t \sin \Omega_0 t. \tag{36}$$

Equation (36) is plotted in fig. 2 together with $|C_2(t)|^2$ for the case $\omega_{12} = 0$. It shows that the dipole moment oscillates at the transition frequency but its size increases and decreases at twice the nutation frequency. When the atom is in a well-defined state $|e\rangle$ or $|g\rangle$ the dipole does not oscillate, there is no emission or absorption at the corresponding times $(t = 0; t = \pi/\Omega_0; t = 2\pi/\Omega_0; \ldots)$.

Up until now we have not introduced losses or damping, so when the external field is suppressed at some intermediate time t, the dipole will continue to oscillate, keeping memory of the mixed state in which it was left when the field was suppressed: the field and the atom infinitely exchange their energy synchronously and elastically at the rate existing at the time of the external field suppression.

This emission is referred to as free induction emission. It is a coherent emission.

2.1.1.3. The pseudo-spin Bloch vector of the two-level system (Haken 1981). By analogy with the Bloch vector of an electron spin interacting with an oscillating magnetic field



Fig. 2. $|C_2(t)|^2$ and $\langle e.d \rangle$ for the resonant case $(\omega_{12}=0)$.

superimposed on a permanent one, we have to introduce at this point the "pseudo-spin Bloch vector" because it is the picture most often referred to in the literature dealing with superfluorescence.

Let us define a "pseudo-spin Bloch vector" by the following coordinates

$$S_1 = -(C_1^* C_2 e^{i\omega_0 t} + C_1 C_2^* e^{-i\omega_0 t}),$$
(37)

$$S_2 = (C_1^* C_2 e^{i\omega_0 t} + C_1 C_2^* e^{-i\omega_0 t}),$$
(38)

$$S_3 = |C_1|^2 - |C_2|^2.$$
(39)

Recalling that $C_2(t) = i \sin \frac{\Omega_0 t}{2}$, and

$$C_1(t) = \cos\frac{\Omega_0 t}{2},\tag{40}$$

it follows that

$$S_1 = \sin \Omega_0 t \sin \omega_0 t, \tag{41}$$



Fig. 3. Locus of the pseudo-spin Bloch vector with time.

$$S_2 = \sin \Omega_0 t \cos \omega_0 t, \tag{42}$$

$$S_3 = \cos \Omega_0 t. \tag{43}$$

The parametric curve described by eqs. (41)-(43) is represented in fig. 3.

Starting from the vertical upright position, the vector S shall reorient to the vertical downward position, its extremity having described a spiral on a sphere in the represented space and it shall reorient up again as time goes on ad infinitum under the external applied field. If the field is suppressed, the vector describes a circle on the sphere according to the Ω_0 existing when the field was suppressed.

Comparison of eqs. (36) and (42) shows that the pseudo-spin Bloch vector can be considered as the unit vector of the dipole electric moment projected on one of the axes of the horizontal plane. This shows that the maximum radiation is obtained when the Bloch vector is in the horizontal plane, which happens for $\Omega_0 t = \frac{1}{2}\pi$. If the field is suppressed at $t = \pi/(2\Omega_0)$ there is a maximum of emission. Such excitation is called a $\frac{1}{2}\pi$ pulse.

Oppositely, a " π pulse" alone would leave a zero-amplitude dipole. Playing such pulses in sequence is the root of the photon-echo process which, however, is not our particular subject here.

2.1.1.4. Spontaneous emission and the Weisskopf-Wigner damping (Weissbluth 1989). Spontaneous emission is characterized by its independence of the initial photon number, that is, n=0. The initial state is $|1\rangle = |e, 0\rangle$, and the final state is $|2\rangle = |g, 1\rangle$. However, $|2\rangle$ is not confined to a single mode because the spontaneous photon can be emitted in any direction with any phase and polarization and we have to sum over all theses modes $(\lambda | 1_{\lambda} \rangle)$ for photon number $|1_{\lambda}\rangle$. Consequently we now have to consider the following versions of eqs. (5) and (6):

$$i\hbar \dot{C}_1(t) = \langle e, 0 | H_{\rm AF} | g, 1_\lambda \rangle C_2(t) e^{i\omega_{12}t}$$
(44)

$$i\hbar\dot{C}_2(t) = \sum_{\lambda} \langle g, 1 | H_{\rm AF} | e, 0 \rangle C_1(t) e^{i\omega_{21}t}.$$
(45)

Solving for $C_1(t)$, we may write

$$\dot{C}_1(t) + \frac{\hbar\Gamma + i\Delta E}{2\hbar}C_1(t) = 0, \tag{46}$$

where

$$\frac{\hbar\Gamma}{2} = \frac{\pi}{\hbar} \sum_{\lambda} \left| \langle g, 1_{\lambda} | H_{\rm AF} | e, 0 \rangle \right|^2 \delta\omega_{12}, \tag{47}$$

and

$$\frac{\Delta E}{2} = \frac{1}{\hbar} \sum_{\lambda} |\langle g, 1_{\lambda} | H_{\rm AF} | e, 0 \rangle|^2 \times \begin{cases} \frac{1}{\omega_{12}} & \text{for } \omega_{12} \neq 0, \\ 0 & \text{for } \omega_{12} = 0. \end{cases}$$
(48)

With the initial conditions (32), the solution for eq. (46) is

$$C_1(t) = e^{-\Gamma t/2} e^{-i\omega 0\Delta E t/2\hbar}, \qquad C_1^2(t) = e^{-\Gamma t}.$$
 (50,51)

So the probability of being in state $|e, 0\rangle$ is a decreasing exponential function with time; the state has a lifetime $\tau_0 = \Gamma^{-1}$ given by eq. (47).

 Γ represents a level width called the "homogeneous natural width" because this width results from the Heisenberg uncertainty relation between time and energy and cannot be reduced.

Equation (48) gives a shift in the energy separation of the atomic level induced by off-resonance photons since it exists only for $\omega_{12} \neq 0$. The experimental shift, however, is much smaller than that given by eq. (48) and can be often neglected.

Equation (47) can be written as

_

$$\Gamma = \frac{2\pi}{\hbar^2} \sum_{\lambda} |\langle g, 1_{\lambda} | H_{\rm AF} | e, 0 \rangle|^2 \, \delta\omega_{12}, \tag{52}$$

which is equivalent to the Golden Rule for spontaneous emission. Replacing the matrix element by its value (23) yields

$$\Gamma = \frac{2\pi}{\hbar^2} \sum_{\lambda} \hbar^2 g^2 (0 + 1_{\lambda}) \,\delta\omega_{12} \tag{53}$$

or for one mode

$$\Gamma_{\lambda} = 2\pi g^2 \delta \omega_{12}. \tag{54}$$

At this point it is interesting to compare this Weisskopf–Wigner damping with what can be obtained from eq. (29). For spontaneous emission n=0, eq. (29) is written

$$C_{2}(t) = \frac{2i|g|}{\Omega} e^{(i/2)(\omega_{0} - \omega)t} \sin \frac{1}{2}\Omega t,$$
(55)

and the corresponding probability is

$$|C_2(t)|^2 = \frac{4g^2}{\Omega^2} \sin^2 \frac{1}{2} \Omega t.$$
 (56)

Let us comment on this apparent oscillatory behavior: we had found Ω by its definition

$$\Omega = \sqrt{\omega_{12}^2 + 4g^2 n^{1/2} (n+1)^{1/2}},\tag{30}$$

which reduces to $\Omega^2 = \omega_{12}^2$ for n=0, showing that at resonance $(\Omega \to 0)$, there is no oscillatory behavior for $C_2^2(t)$ in spontaneous emission. This is at variance with the result of Allen and Eberly (1975) giving

$$\Omega^2 = \omega_{12}^2 + 4g^2(n+1) \tag{57}$$

(in fact assuming a spontaneous absorption), which for spontaneous emission and resonance reduces to $\Omega_0^2 = 4g^2$, the semi-classical result.

Although the contrary is stated by Allen and Eberly (1975), the results of Jaynes and Cummings (1963) as well as the results of Weissbluth (1989) give a non-oscillatory behavior:

$$\Omega^2 = \omega_{12}^2 + 4g^2 n, \tag{58}$$

which is slightly different from eq. (30).

What we can say is that at exact resonance, spontaneous emission by itself keeps no memory at all of the atomic wave functions. Off-resonance these still have a slight influence through the detuning ω_{12} . On the other hand, eq. (56) with $\Omega \rightarrow 0$, reminds us of the Golden Rule formulation

$$\lim_{\Omega \to 0} |C_2|^2(t) = 4g^2 \frac{1}{2}\pi t \,\delta\omega_{12},\tag{59}$$

or

$$W_{\rm spont.} = 2\pi g^2 \,\delta\omega_{12},\tag{60}$$

which is just the spontaneous emission probability per unit time for one mode, as given by eq. (54). So, the fully quantized Rabi equation gives the same result for spontaneous emission as the Weisskopf-Wigner approach. By summing eq. (60) over all modes and polarization, one has, from eq. (19),

$$W_{\rm spont} = \frac{\omega^3}{3\pi c^3 \hbar \varepsilon_0} \left| \langle d \rangle \right|^2 = \frac{4\alpha \omega^3}{3c^2} \left| \langle r \rangle \right|^2, \tag{61}$$

where α is the fine structure constant,

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137},$$

and d=e.r is the dipole moment. Equation (61) is just the well-known Einstein A coefficient for spontaneous emission.

2.1.2. Merging of coherent emission and spontaneous decay

2.1.2.1. Damping of Rabi oscillation by spontaneous decay. We have just seen that the effect of the coupling of the atom with all the modes of the empty field is to introduce a damping constant. Neglecting the spontaneous emission shift ΔE , eq. (50) can be written as

$$C_1(t) \cong e^{-(\Gamma_1/2)t},$$
 (62)

or:

$$i\hbar\dot{C}_1(t) = -\frac{1}{2}i\hbar\Gamma_1 C_1(t).$$
 (63)

Then a general form for the Schrödinger equation (4) with damping can be written:

$$i\hbar\dot{C}_{1}(t) = \sum_{k} C_{k}(t) \langle \phi_{1}(r) | V(t) | \phi_{k}(r) \rangle e^{i\omega_{1k}t} - \frac{1}{2}i\hbar\Gamma_{1} C_{1}(t).$$
(63')

For our two-level system, eqs. (26) and (27) yield

$$i\hbar \dot{C}_1(t) = C_2(t)\hbar g\sqrt{n} e^{i\omega_{12}t},$$
(64)

$$i\hbar \dot{C}_{1}(t) = C_{2}(t)\hbar g\sqrt{n} e^{i\omega_{21}t} - \frac{1}{2}i\hbar\Gamma_{2}C_{2}(t),$$
(65)

where 1 has been removed from (n+1) since, as we saw above, Γ_2 replaced it. Stating that

$$C_2' = C_2 \mathrm{e}^{-\Gamma_2 t/2}$$

the system (64), (65) gives a new form for the Rabi frequency:

$$\boldsymbol{\varOmega} = \left(\omega_{21} - \frac{1}{2}\mathbf{i}\boldsymbol{\Gamma}_2\right) + 4g^2\boldsymbol{n},\tag{66}$$

and

$$C_2(t) = \frac{i2g\sqrt{n}}{\Omega} e^{(i/2)(\omega_{21})t} e^{-(\Gamma_2/2)t} \sin\frac{1}{2}\Omega t,$$
(67)

and for the probability we get

$$|C_2(t)|^2 = \frac{4g^2n}{\Omega^2} e^{-\Gamma_2 t} \sin^2 \frac{1}{2} \Omega t.$$
 (68)

This shows that spontaneous emission can be viewed as a damping of the Rabi oscillation. Remembering that the Rabi oscillation persists after the external field has been removed,



one can see that the basic fact is that the coherence still existing after the removal of the field is the one not yet destroyed by spontaneous emission, as shown by fig. 4.

In the Bloch vector representation, this means that instead of circling ad infinitum on a parallel of the sphere of fig. 3, the Bloch vector spirals down with vertical damped oscillation. In case the Bloch vector would fall down without spiraling there would be no coherence left at all. This possibility for a coherence (free induction) is the root of superradiance and superfluorescence.

However, it should be noted that there is no general solution for the problem of the movement of the damped Bloch vector (Allen and Eberly 1975). So in general, the Bloch sphere is considered only for time $t \ll 1/\Gamma$.

2.1.2.2. The link between the various relaxation times. Returning to the pseudo-spin Bloch vector, its motion of nutation given by eqs. (41)-(43) in the absence of damping, shows us that it can be described by an equation of the form

$$\dot{\boldsymbol{S}} = \boldsymbol{\Omega} \wedge \boldsymbol{S},\tag{69}$$

where Ω is the rotation-vector axis around which S nutates. The coordinates of Ω are $(\Omega_0, 0, \omega_{12})$. Equation (69) is the "Bloch equation" without damping. Damping has been introduced phenomenologically by Bloch in the following form

$$\dot{\mathbf{S}} = (\mathbf{\Omega} \wedge \mathbf{S}) - [\mathbf{S} - \boldsymbol{\delta}(1, i)] \mathbf{T}^{-1} \qquad i = 1, 2,$$
(70)

with T having the coordinates (T_2, T_2, T_1) . T_2 is the so-called "Bloch transverse relaxation time"; it characterizes perturbations on the phase of the dipole, not on its energy. T_1 is the "Bloch longitudinal relaxation time"; it characterizes perturbations on the energy of the system. The names come from the fact that T_2 applies to movement perpendicular to Ω whereas T_1 applies to the movement longitudinal with Ω .

F. AUZEL

In case the only damping is spontaneous emission, one can see from the definition of S in eqs. (37)-(39) that the damping on S_3 comes from $|C_1(t)|^2$ and so is just the Γ given by eqs. (51) and (53). Then T_1 can be identified with τ_0 , the spontaneous radiative lifetime.

From their definitions, S_1 and S_2 are directly linked with the $C_2(t)$, not with their square; the corresponding damping then is $\Gamma/2$, and one has

$$\frac{\Gamma}{2} = \frac{1}{T_2},\tag{71}$$

and then

$$\frac{1}{T_2} = \frac{1}{2T_1}.$$
(72)

Also, because S_1 , S_2 are given by products $C_1^*(t) \cdot C_k(t)$, the phase of $C_1(t)$ plays a role, and T_2 , being linked with this phase, is called the dephasing time.

Up to now we have been dealing with one atom and the field. In the real world we shall have several atoms or ions and there will be ion-ion and ion-phonon interactions, contributing to T_2 in addition to the contribution from T_1 ; also there will be ions in different surroundings with an inhomogeneous spread of energies ω_0 contributing to the dephasing time. Then generally T_2 will be written as

$$\frac{1}{T_2} = \frac{1}{T'_2} + \frac{1}{T^*_2}, \quad \text{and} \quad \frac{1}{T_2} > \frac{1}{T_1},$$
(73)

affecting all atoms homogeneously, where $1/T_2^*$ is the inhomogeneous contribution to the dephasing of the atom-field interaction. This dephasing comes from the $\omega_{12} \neq 0$ case as shown in fig. 1.

2.1.3. Field-coupled cooperative multi-ion effects

Having looked in some detail at the single-atom-field interaction, the very root of coherent emissions, we shall in the following consider cooperative multi-ion effects, staying at the "lowest level of subtlety" (Allen and Eberly 1975). The higher level of subtlety may be found in articles by Bonifacio and Lugiato (1975), Allen and Eberly (1975), Stenholm (1973), and Gross and Haroche (1982), where the construction of the multi-ion system into Dieke states (Dieke 1954) is analyzed, where the statistical dynamics of the whole system is considered through the density matrix dynamics, and where propagation of the interacting field at retarded time is taken into account.

In the following, after using the definition of Bonifacio and Lugiato (1975) for superradiance and superfluorescence, we shall give the few existing examples of such effects in solids and R-doped systems; most of the first experiments on superradiance had been demonstrated on gaseous systems. 2.1.3.1. Superradiance. We consider a system of several two-level atoms occupying a volume the dimension of which is small compared to λ^3 . In this case the total radiating dipole is given by eq. (36), multiplied by the difference of atom populations in the excited state and in the ground state. If the external resonant field is stopped at $t = \pi/2\Omega_0$, we shall create a "macro dipole" given by:

$$\langle M \rangle = (N_1 - N_2) \frac{1}{2} \hbar \Omega_0 \sin \omega_0 t, \tag{74}$$

where $(N_1 - N_2)$ is the population inversion per unit volume. The power radiated per unit volume by this dipole is

$$P = \overline{E(t) \frac{\mathrm{d} \langle M \rangle}{\mathrm{d}t}}, \qquad P = \omega_0 \left(N_1 - N_2 \right) \frac{1}{2} \hbar \Omega_0 E_0 \overline{\cos^2 \omega_0 t}, \qquad (75,76)$$

where $E(t) = E_0 \cos \omega_0 t$ is then the "reaction field", that is, the field created by the oscillating dipole itself after the externally applied field has been suppressed. If the small cavity we are considering has a quality factor Q, the field inside, given by the power P is (Hill et al. 1967)

$$E_0^2 = \frac{8\pi QP}{\omega},\tag{77}$$

and combining eqs. (76) and (77) gives

$$P = \pi Q \omega (N_1 - N_2)^2 \frac{1}{2} \hbar^2 \Omega_0^2$$
(78)

or:

$$P = \omega \pi Q (N_1 - N_2)^2 \hbar^2 g^2 n$$
⁽⁷⁹⁾

in terms of the dipole matrix element of the atomic transition $\hbar g$.

The square dependence of emitted power on inversion density $(N_1 - N_2)$ is typical of the coherence of the multi-atom emission. It is typical of superradiance as well, and, as we shall see, of superfluorescence.

Equation (79) holds as long as coherence between atoms is not destroyed by spontaneous decay or other dephasing processes. The synchronism of the many atoms involved, is obtained by the coherent pumping pulse, directly exciting the emitting level; in Bonifacio's definition this is superradiance, the ordering being obtained by the coherence of the pump. In the language of Allen and Eberly (1975) this would be "passive superradiance" to distinguish it from "active superradiance" where the ordering of the many atoms emission is obtained by their common reaction field. Such a case is called "limited superradiance" by MacGillivray and Feld (1976) as opposed to "strong superradiance" first reported in 1973 in optically pumped HF gas (Skribanowitz et al. 1973). In this case all the energy stored in the sample is emitted cooperatively and so

the decay is dramatically accelerated. However, since the macro-dipole was not created by the pump but rather by the reaction field, it was recognized later to be a case of superfluorescence (Polder et al. 1979) as shall be described in the next section.

So the first example of real superradiance was in fact the free induction decay and the decay of the photon echo observed in ruby by Kurnit, Abella and Hartmann (1964). When a $\frac{1}{2}\pi$ pulse from a ruby laser was sent onto a ruby crystal, the free induction decay and the echo decay observed were about 50 ns, when compared to the usual Cr³⁺ radiative decay time of 4 ms, showing clearly the radiation emission from the macro-dipole.

Returning to eq. (79) we may try to estimate the new decay time resulting from the cooperative emission in strong superradiance. Such a decay time is also called "superradiant lifetime" and its inverse is called "radiative damping constant". Calculating this lifetime as (Yariv 1967)

$$\tau_{\rm SR} = \frac{\text{stored energy by inversion}}{\text{radiated power}}$$

it follows from eq. (79) that

$$\tau_{\rm SR} = \frac{2(N_1 - N_2)\hbar\omega}{\omega\pi Q(N_1 - N_2)^2\hbar^2 g^2 n} = \frac{2}{\omega\pi Q(N_1 - N_2)\hbar g^2 n}.$$
(80)

According to eq. (60) $2\pi g^2 \delta \omega_{12} = \tau_0^{-1}$ is the spontaneous decay for one mode, thus

$$\tau_{\rm SR} = \frac{4\tau_0}{Q(N_1 - N_2)\hbar n} \delta\omega_{12} = \frac{4\tau_0}{Q(N_1 - N_2)n} \delta E_{12}.$$
(81)

This shows that, everything else being kept constant, the spontaneous lifetime is reduced in proportion to the initial population inversion.

According to geometric conditions for preparation of the excited state of the whole sample, several modes may be allowed to emit, and partial summation over them has to be done in eq. (81).

Since the macro-dipole exists right after excitation, the superradiance shortened decay starts without delay, beginning with the $(N_1 - N_2)^2$ behavior. The only condition is that the dephasing rate is slower than the superradiant one so that the macro-dipole keeps on existing during the transition, that is

$$\frac{1}{\tau_{\rm SR}} > \frac{1}{T_2}.$$
(82)

In the optical frequency domain, superradiance in the Dieke and Bonifacio sense (Dieke 1954, Bonifacio and Lugiato 1975), i.e. with strong radiation damping, seems to have been observed in solids up to now only in photon-echo experiments, as already mentioned. The difficulty lies in the preparation of the macro-dipole in a volume smaller than λ^3 . However the recent interest in restrained geometry, e.g. the so called 2D, 1D

and 0D geometries, allows the construction of microscopic structures with volume $<\lambda^3$ and so we suspect it could be observed, because spontaneous emission is then enhanced (Yamamoto et al. 1991).

2.1.3.2. Superfluorescence (SF).

2.1.3.2.1. The basic process. Contrary to the previous case we will now consider the cooperative emission of a large number of initially inverted atoms, without an initial macroscopic dipole moment left by the excitation pulse. It means that instead of excitation by a $\frac{1}{2}\pi$ pulse creating Dieke states, excitation is performed by a π pulse, leaving the pseudo-spin Bloch vector initially along Ω . Each atom is in its upper excited state and the whole sample is inverted (fig. 3).

Preparation of excitation does not need coherence, and in experiments a phononemitting step can be used to obtain inversion. Fluctuation in spontaneous emission allows the beginning of the effect, with initially the spontaneous lifetime τ_0 of individual atoms and with an emitted power proportional to the inverted atoms number N. After a delay t_d the whole system starts radiating coherently with a power proportional to N^2 , and the reduced decay time is τ_0/N analogous to superradiance. Except at its initial stage, superfluorescence is equivalent to superradiance; it is a self-organized superradiance. Self-organization can be viewed as induced by the field. This initial interaction between two atoms is depicted in fig. 5. The building up of the far field of a system of 10^4 individual Bloch vectors has been simulated (Schwan 1991); the result is given in fig. 6 for increasing steps in time. The weak field emitted by ordinary fluorescence produces a weak polarization of the medium, increasing the field which in turn increases polarization and so on up to the superradiant emission. The macroscopic dipole has been spontaneously created by the self-organization of the system alone and not by an external coherent pump.

It was recognized that a macroscopic pencil-shaped sample with length $\gg \lambda$ could be used (Bonifacio and Lugiato 1975) which opens the way to experiments in gases at optical frequencies (Skribanowitz et al. 1973), and also to the first demonstration (Florian et al. 1982) of this effect in a solid.



Fig. 5. Interaction of two Bloch vectors through their spontaneous electromagnetic field (after Schwan 1991).



Fig. 6. Simulated far field created by a horizontal sheet of 2-level inverted atoms at various steps (n) in time (after Schwan 1991).

In order to calculate the superfluorescent collective lifetime, we just say that the new rate $(N/\tau_{\rm SF})$ is given by the square law behavior of eq. (79) (Stenholm 1973)

$$N\frac{1}{\tau_{\rm SF}} \equiv N^2 \frac{1}{\tau_0} \frac{\mathrm{d}\Omega}{\int \Omega}.$$
(83)

where $d\Omega$ is the solid angle corresponding to the diffraction lobe of the end surface (S) of the pencil-shaped sample into which emission is directed; that is (Schuurmans 1980)

$$\frac{\mathrm{d}\Omega}{\int \mathrm{d}\Omega} = \frac{\lambda_0^2/S}{8\pi/3}.$$
(84)

Combining eqs. (83) and (84) yields

$$\tau_{\rm SF} = \frac{8\pi S}{3N\lambda_0^2} \tau_0. \tag{85}$$

This is analogous to the result (81) found for superradiance in a microcavity. Let $\rho = N/C$ be the density of inverted atoms; it then follows that

$$\tau_{\rm SF} = \frac{8\pi}{3\rho} \frac{\tau_0}{L\lambda_0^2},\tag{86}$$

the most widely used formula for the superfluorescent lifetime (Bonifacio and Lugiato 1975, Schuurmans 1980, Malcuit et al. 1987) in terms of the spontaneous atom lifetime (τ_0) for the considered transition.

Equation (84) assumes that the diffraction angle λ_0^2/S equals the geometric solid angle S/L^2 which corresponds to a Fresnel number

$$F = \frac{S}{\lambda_0 L} \cong 1. \tag{87}$$

The problem can then be treated as being one-dimensional, with two plane waves building up backwards and forwards, taking into account propagation (Schuurmans 1980).

The physical process of self-organization takes some time corresponding to a delay given, according to different calculations, either by (Schuurmans 1980)

$$t_{\rm d} = \frac{\tau_{\rm SF}}{16} \left[\ln 2\pi N \right]^2, \tag{88}$$

or by (Schuurmans and Polder 1979)

$$t_{\rm d} = \frac{\tau_{\rm SF}}{4} [\ln(2\pi N)^{1/2}],\tag{89}$$

or by (MacGillivray and Feld 1976)

$$t_{\rm d} = \frac{\tau_{\rm SF}}{4} \left[\ln(\theta_0) \right]^2,\tag{90}$$

where θ_0 has the "physical" meaning of the "initial tipping angle" of the Bloch vector in the vertical metastable position as an effect of the vacuum field fluctuation initiating spontaneous decay. It is found to be given by $\theta_0 \cong 2N^{-1/2}$ (Malikov and Trifonov 1984). Equations (88)–(90) show that t_d is linearly linked with τ_{SF} and that the delay is reduced when N is increased since τ_{SF} decreases more strongly than the logarithmic function (eq. (85)). Practically, τ_{SF} is one or two orders of magnitude smaller than t_d .

Since now we have a large sample, atoms have to be able to interact by their field faster than they can radiate. This condition fixes an upper limit to the increase in the SF rate with the number of inverted atoms N, as given by eq. (85). When an atom emits at the rate $1/\tau_c$, it emits a wave train of length

 $l_{\rm c} = c \tau_{\rm c}.\tag{91}$

When there is coherence in the wave front over the whole end surface of the sample, the wave train shall interact with a maximum of N_c atoms, where N_c is given by the following expression

$$N_{\rm c} = l_{\rm c} S \rho. \tag{92}$$

From eq. (85) we also have

$$\tau_{\rm SF} = \frac{8\pi}{3N_{\rm c}} \frac{S}{\lambda_0^2} \tau_0. \tag{93}$$

From eqs. (91)–(93) we get

$$\tau_{\rm c} = \sqrt{\frac{8\pi}{3C} \frac{\tau_0}{\rho \lambda^2}},\tag{94}$$

introducing the photon lifetime in the entire sample, the escape time $\tau_{\rm E}$

$$\tau_{\rm E} = L/c. \tag{95}$$

Using eq. (86) we write eq. (94) as

$$\tau_{\rm c} = \sqrt{t_{\rm SF} \tau_{\rm E}},\tag{96}$$

which is the so-called "Arecchi–Courtens cooperation time" (Arrechi and Courtens 1970); l_c is the corresponding critical cooperation distance.

2.1.3.2.2. The conditions for SF. Having built them step by step, we now have all the elements necessary for SF. The conditions for dephasing already stated for SR (eq. 82) may be extended to all dephasing times T_1 , T'_2 , T^*_2 , whichever is the shortest, as

$$\tau_{\rm SF} < T_1, \ T_2', \ T_2^*. \tag{97}$$

Since the phase has to be conserved also during the self-synchronization step, we have

$$t_{\rm d} < T_1, \ T_2', \ T_2^*.$$
 (98)

Equation (85) gave us the shortest possible τ_{SF} as τ_c which is intermediate between τ_E and τ_{SF} (eq. 96). To sum up, we have

$$\tau_{\rm E} < \tau_{\rm c} < \tau_{\rm SF} < \tau_{\rm d} < T_1, \ T_2', \ T_2^*, \tag{99}$$

giving the conditions for SF. Conditions (99) have been stated in simpler form (Bonifacio and Lugiato 1975) as

$$L_{\rm T} \ll L \ll l_{\rm c},\tag{100}$$

where $L_{\rm T}$ is a threshold length for SF given by

$$L_{\rm T} = \alpha^{-1}, \qquad \alpha = \frac{T_2}{L\tau_{\rm SF}}.$$
 (101)

Equation (101) is equivalent to $L\tau_{\rm SF}/T_2 \ll L$ or $\tau_{\rm SF} \ll T_2$. This condition also implies

$$\alpha L = \frac{T_2}{\tau_{\rm SF}} \gg 1,\tag{102}$$

which is the "large-gain" or "large-absorption" condition of Friedberg and Hartmann (1971).

2.1.4. Experimental results for superradiance and superfluorescence in rare-earth (R) ion systems

2.1.4.1. Superradiance (SR) and R ions. We have seen that superradiance (SR) in solids with radiation damping has been observed in ruby as the accelerated free induction decay of a photon echo experiment (Kurnit et al. 1964). Since then many free induction decay and photon echo experiments have been conducted in Pr^{3+} -doped systems in order to reach the homogeneous width through a T_2 measurement ($\Delta v_{\text{hom }o} = (2\pi T_2)^{-1}$) (Genack et al. 1976, Shelby and Macfarlane 1984, De Voe and Brewer 1983), and in Ho³⁺ and Er³⁺-doped fluorides (Wannemacher et al. 1990, Macfarlane and Shelby 1982).

For instance LaF₃:Pr³⁺ (${}^{3}H_{4}(\Gamma_{1}) \rightarrow {}^{1}D_{2}(\Gamma_{2})$ transition) at 2K, shows a homogeneous linewidth as small as 56 KHz (T_{2} = 5.6 µs) under the Earth's magnetic field, going down to 4.1 KHz and a T_{2} as long as 77 µs under a radio frequency averaging field (Macfarlane et al. 1980). This T_{2} sensitivity to the magnetic field indicates that the principal dephasing process in R at low temperature is linked to ligand–R and dipole–dipole interaction. Macfarlane and Shelby (1987) and Macfarlane (1992) have recently reviewed these experiments in which R ions are coherently prepared giving rise to coherent emissions. However the results do not show, as for ruby, the presence of radiation damping which would indicate the collective effect of superradiance. In such experiments pumping intensity and the Rabi frequency were deliberately kept low in order to reach the largest T_{2} and the ultimate homogeneous width. So we believe SR emission has not yet been observed in R-doped systems.

2.1.4.2. Superfluorescence (SF) in the solid state and in R ions. Because even the radiation damping of the free induction decay in ruby (Kurnit et al. 1964), has been questioned as being SR and reinterpreted as a superfluorescence emission (Polder et al. 1979), SF seems easier to observe, so let us review the situation in R-doped systems.

In solids up to now, only a few cases of SF have been observed. This arises from the difficulty to obtain long T_2 , because in a solid, active centers may be subjected to many perturbations: multiphonon decays and ion-ion energy transfers in addition to inhomogeneous contribution and the strong spontaneous radiative decay at optical frequencies. In gas, it has been assumed that in order to avoid dipole-dipole interactions, the atom density should fulfil (Polder et al. 1979)

$$\rho\left(\frac{\lambda_0}{2\pi}\right)^3 \ll 1. \tag{103}$$

This condition means that there should be less than one atom per one wavelength volume. In a solid this is never the case. Fortunately we know that dipole-dipole energy transfers between ions in the absence of clusters are important only when they are separated by less than about 20 Å in the case of trivalent R ions with oscillator strength $f \approx 10^{-6}$. For a stronger transition, this distance may be enlarged. It means that higher concentrations are possible in solids and consequently the sample may have smaller dimensions than for experiments in gases.


Fig. 7. ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ emission of LiYF₄:Er³⁺ at 10 K for 70 mW (solid line) and 144 mW (dashed line) incident power at 0.64 µm (Auzel et al. 1988a).

The first observation of SF in the solid phase was obtained by Florian, Schwan and Schmid (1982) in KCl:O₂⁻. Emission was observed in the visible at 0.63 μ m under 30 μ J of 0.265 μ m excitation focused on 10 μ m diameter (100 MW cm⁻²) with sample temperatures of 10–30 K. 5 mm³ size samples were doped with 0.5% KO₂⁻. Many characteristics of SF have been observed (Florian et al. 1984, Schiller et al. 1987): line emission narrowing, directivity, threshold, pulse delay behavior. Also the excitation is through phonon emission steps which preclude the coherent excitation of SR. The same effect has also been observed by these authors in KBr:O₂⁻ and KI:O₂⁻.

Emission is distinguished from amplification by stimulated emission (ASE) (see sect. 2.2) because it is independent of orientation of the crystal with respect to the pumping beam; and even Brewster incidence is used to prevent Fresnel reflection on the extremities (Schiller et al. 1987). Also no longitudinal mode structure is observed as would be expected in a laser; all these facts point to SF rather than to an ASE process.

Recently the smooth evolution from SF to ASE in the same KCl:O₂⁻ system, has been investigated by raising the temperature slowly from 10 to 30 K, thus increasing the dephasing rate T_2 (Malcuit et al. 1987); the criterion studied was that of Schuurmans and Polder (1979) (sect. 2.2.1, eqs. 106 and 107).



Fig. 8. Emission intensity at $2.72 \,\mu\text{m}$ vs. pump incident power on $\text{LiYF}_4:\text{Er}^{3+}$ (Auzel et al. 1988a).

So the first observation of SF in the solid phase showed all the typical features one has to look for in such a process.

A theoretical investigation by Malikov and Trifonov (1984) for YAG:Nd at 100 K showed that if superradiance was possible, superfluorescence could not be observed in such a system, because it would be three orders of magnitude less intense than ordinary fluorescence. Calculations were based on a $T_2 = 17$ ps and $\alpha L = 5$ for an inversion density of 10^{16} cm⁻³. Superradiance could be obtained by the propagation of a short coherent pulse which could provide pulses with $\tau_{SR} = 3$ ps.

However, the first superfluorescence effect in a R-doped system seems to have been observed recently (Auzel et al. 1988a) under very low CW excitation, much below $1 \,\mathrm{kW} \,\mathrm{cm}^{-2}$. In this experiment the sample was a single crystal of $\mathrm{LiYF_4:1\%Er^{3+}}$ of thickness 1.5 mm with two unparallel unpolished (as cut by a diamond saw) faces, so that no Fresnel reflection optical feedback was likely to occur. Excitation was obtained by a CW krypton laser with a line at 6470 Å allowing up to 320 mW of incident power on the sample as measured by a pyroelectric radiometer. The pump focalization gave a beam waist diameter of 110 μ m. Luminescence was observed in the backward direction with a lens system focalizing the sample output face on a monochromator. A room temperature PbS photoresistor was used to detect the 2.7 μ m emission. Direct recording of the PbS cell output on an oscilloscope allowed inspection of the temporal behavior of emission.

Below about 80 mW of incident power (842 W cm⁻²) with sample at 10 K, emission spectra for the ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ transition are as shown in fig. 7; above this threshold observed spectra peaked only at 2.72 µm, showing clearly a spectral narrowing. Output intensity vs. incident pump power is shown in fig. 8 on a log–log scale. There is a marked threshold, then emission follows a square law vs. pump power. When the temperature



Fig. 9. Temporal behavior of LiYF₄:Er³⁺ (a) just above threshold; (b) well above threshold; (c) at threshold showing both SF (spikes) and spontaneous emission ($\tau_0 \approx 4 \text{ ms}$) (Auzel et al. 1988a).

is increased up to about 40 K, the threshold increases up to the 320 mW available for pumping. Because of the mismatch between the krypton line at 6470 Å and the $Er^{3+} {}^{4}I_{15/2} \rightarrow {}^{4}F_{9/2}$ transition, and of the low Er^{3+} concentration, the 80 mW threshold corresponds to only 2.8 mW of absorbed power.

Figure 9a shows the temporal behavior obtained under a quasi-CW excitation square pulse of \sim 50 ms duration just above threshold (107 mW of incident pumping); fig. 9b shows the temporal behavior for emission well above threshold (320 mW incident). Raising the temperature up to 38K it was possible to obtain the behavior just at the threshold (210 mW incident) (fig. 9c).

The measured τ_{SF} was later found to be detector limited; using an Hg–Cd–Te (77K) detector with a response of 120 ns, τ_{SF} was measured to be 150 ns (Hubert et al. 1990). A pulsed excitation could provide in some cases a single pulse emission as shown in fig. 10.

In a systematic study of the threshold with temperature it was found that this effect could not be observed for T > 60 K and that for a given concentration the threshold



Fig. 10. Single SF pulse emission of LiYF_4 :Er³⁺ under pulse excitation (PbS detector).



Fig. 11. Exponential behavior for SF threshold with temperature in $LiYF_4:Er^{3+}$ (Hubert et al. 1990).

value behaves exponentially, as shown in fig. 11, with an activation energy of 14 cm^{-1} , corresponding to the first Stark splitting of the ${}^{4}I_{11/2}$ excited state.

Contrary to the laser action which could be obtained at room temperature with a concentration of $Er^{3+} = 15\%$ (Auzel et al. 1989a), a rather weak Er^{3+} concentration of <5% is required for SF. So we may now list all the arguments in favor of SF in R experiments and which are at variance with ASE as we shall see in sect. 2.2:

(1)
$$\rho^2$$
 dependence;

(2) $\tau_{\rm SF} < 150 \,\mathrm{ns}$ to be compared to a T_2 of about 300 ns up to 2 µs (Lin et al. 1987) for R in such a crystal at low temperatures. It has been pointed out that one should consider an effective T_2 (Skribanowitz et al. 1973) given by

$$T_2^{\text{eff}} = \alpha L T_2^*,\tag{104}$$

in systems where $\alpha L \ge 1$. Then condition (102) becomes

$$\alpha L = \frac{\alpha L T_2^*}{\tau_{\rm SF}}$$

or

$$T_2^* \geqslant \tau_{\rm SF},\tag{105}$$

which is much less stringent than eq. (102) when dephasing is governed by inhomogeneous broadening as is probably the case;

- (3) the effect has been observed on very short length samples down to $100 \,\mu\text{m}$ though the concentration was $\leq 1\%$. ASE would rather require the opposite;
- (4) the effect needs a weak concentration, pointing also to the requirement of a reduced ion-ion dephasing;
- (5) the temperature behavior points also to the involvement of a T_2 variation temperature effect.

2.1.4.3. SF applications. Since no mirrors, with of course limited transparency, are needed for SF, it is in principle the most efficient process to produce very narrow pulses of coherent light. In the frequency range where mirrors are difficult to produce it could be the only way to obtain coherent sources: such would be the case for X-rays and γ -rays. However the drawback is that the spontaneous lifetime of individual atoms becomes very short due to its ν^{-3} dependence and this is probably the most important cause of dephasing.

A more realistic application may be to use it in "triggering spectroscopy" (Carlson et al. 1980), where by injecting a weak resonant field on a prepared SF sample, a large change can be induced in the delay and spatial pattern of the emission. By measuring the change in the direction of the emission lobes as a function of the injection field frequency the transition of ${}^{7}P_{3/2}-{}^{7}S_{1/2}$ of cesium has been recorded with only a few photons per pulse; experimentally the spectrum could be recorded down to 8 nW mm^{-2} .

Along the same lines, one could imagine an Er^{3+} -based solid state amplifier at 2.7 μ m for which a noise figure below the spontaneous emission noise limit of 3 dB could be expected, because noise becomes organized by the signal when it is used to trigger SF.

2.2. Amplification of spontaneous emission by stimulated emission and the laser effect

2.2.1. Amplified spontaneous emission (ASE)

ASE is what happens when a long medium with inverted atoms starts amplifying by stimulated emission the spontaneous emission noise of some atoms at the medium extremity. In such a case all atoms of the medium behave individually and there is no self-building of a macroscopic dipole. Then the intensity remains proportional to N or ρ , instead of N_2 and ρ^2 for SF. Also there is practically no delay, since there is no need for building up the dipole.

If the number of excited atoms is sufficiently large, ASE emission is still more rapid than single-atom spontaneous emission, because the spontaneous emission is amplified as the radiation propagates. Because of the long shape geometry, radiation is also directional.

536

The difference with SF stems, in ASE, from the existence of a stronger dephasing which inhibits the self-organization into a macro-dipole.

Schuurmans and Polder (1979) have given the condition on T_2 at which the transition between these two types of behavior occurs.

$$T_2 \gg \sqrt{\tau_{\rm SF} t_{\rm d}},$$
 SF predominates, (106)
 $\tau_{\rm SF} \ll T_2 \ll \sqrt{\tau_{\rm SF} t_{\rm d}},$ ASE predominates. (107)

Also in a very long medium, as in a laser cavity, the conditions on escape time τ_E and on τ_c are not required. In the usual laser amplifiers the condition holds:

$$T_2 \ll \tau_{\rm E},\tag{108}$$

which is opposite to part of eq. (99).

2.2.2. Examples of ASE in R-doped media in comparison with SF

2.2.2.1. ASE in doped fibers. Unlike the SF observations reported in sect. 2.1.4, typical ASE is obtained for the same transition of Er^{3+} at 2.7 µm in 3 m long fluoride fibers at 300 K (Ronarc'h et al. 1991a) (fig. 12). The line narrowing is smoothly obtained when the pump is increased without any threshold. The narrowing would follow a law of the type

$$G(\mathbf{v}) = g(\mathbf{v}) \exp g(\mathbf{v})L,\tag{109}$$

where g(v) is the ordinary fluorescence spectrum line shape. In doped fibers this is so general that the real spectrum shape can be obtained only by looking transversely to the fiber axis to prevent any amplification effect. Many fiber studies for amplification in communications applications have considered ASE and have been recently reviewed in detail (Digonnet 1993, Desurvire 1994, Becker et al. 1996). ASE is then sometimes called superluminescence or even superfluorescence but in neither case it is real superfluorescence as defined in sect. 2.1.3.



Fig. 12. (a) Normal fluorescence obtained on a small bulk sample of Er^{3+} ZBLAN glass; (b) spectrum obtained on the same glass drawn into a 3 m long fiber.

2.2.2.2. ASE in R-doped powders. The difficulty in observing SF in R-doped systems seemed to us confirmed by the ASE experiments of Markushev et al. (1986) on microcrystalline powder of $(MoO_4)_4Na_5Nd$. They obtained, under 30 ns pulsed excitation, all the characteristics of ASE (narrowed spectrum, linear dependence of output with ρ) at a threshold of 1.8 MW cm⁻² at 77 K. Probably because of the very high concentration of active ions (~5–10²¹ cm⁻³), ion–ion interaction had reduced T_2 in a very effective way, thus preventing the construction of the macro-dipole for SF.

Under high excitation, spontaneous decay $T_{\rm I}$ is overtaken also by stimulated emission and the decay time is now $\tau_{\rm E}$, which can even overtake the non-radiative decay ($W_{\rm NR}$) linked with strong electron-phonon interactions:

$$\tau_{\rm E}^{-1} > W_{\rm NR}.\tag{110}$$

A striking example of such overtaking of radiative decay over the non-radiative one has recently been observed (Gouedard et al. 1991, Gouedard et al. 1993). It is known that anhydrous lanthanide chlorides are low threshold laser materials, for instance CeCl₃:Nd³⁺ (Singh et al. 1975a,b), and that NdCl₃, having a low crystal field, would be a weak selfquenching type like the pentaphosphates (Auzel 1979). However hydrated chloride like NdCl₃:6H₂O is expected to show a strong multivibration quenching by coupling of Nd³⁺ with the OH⁻ vibration (Dexpert-Ghys and Auzel 1984). This is confirmed by the very short fluorescent decay time of ~16 ns at 1.05 μ m (fig. 13), obtained when NdCl₃:6H₂O powder is irradiated with pulses from a frequency doubled YAG:Nd³⁺ laser at levels of a few MW cm⁻² at 0.53 μ m. The fluorescent material. The lifetime, compared with the anhydrous value (~1710 μ s), is essentially governed by the non-radiative rate (W_{NR}). Then we have $W_{NR} = 1/(16 \times 10^{-9}) = 6.2 \times 10^7 \text{ s}^{-1}$.

This measured non-radiative rate is consistent with what can be estimated from calculation of a multivibration rate in the "large molecule model" of Haas and Stein



Fig. 13. Emission at $1.054 \,\mu\text{m}$ of NdCl₃:6H₂O powder under a strong pulse excitation below and above threshold (300 K) (Gouedard et al. 1991).

(1974). For a small number of simultaneous vibrations and $6(OH)^-$ species coupled to one Nd³⁺ (Haas and Stein 1974) (see sect. 3.2),

$$W_{\rm NR} \approx 6 \times 10^7 e^{-S_0} \frac{S_0(N-2)}{(N-2)}!.$$
 (111)

Assuming the electron-coupling constant $S_0 \approx 10^{-2}$ (Dexpert-Ghys and Auzel 1984), and N the number of simultaneous vibrations spanning the electronic energy gap ${}^{4}F_{3/2}$ - ${}^{4}I_{15/2}$ of Nd³⁺, as roughly twice one (OH)⁻ vibrational quantum $W_{NR} \cong 6 \times 10^{7} \text{ s}^{-1}$. Equation (111) is a refined version (Auzel 1978) of eq. (129) of sect. 3.2.

Although this good fit is certainly fortuitous due to the many approximations behind it, it shows that the non-radiative properties behave as expected. However, when pumping is increased to 1 GW cm^{-2} level, a threshold is reached where a strong, narrowed and shortened emission at 1.054 µm is observed (fig. 13). This points to the existence of some feedback, probably provided by total reflection at grain boundary: some partial laser action then takes place (see sect. 2.2.3.).

The observed radiative rate (109 s^{-1}) then overtakes the nonradiative one by nearly two orders of magnitude, which in turn allows condition (110) to be more completely fulfilled. So we see that this particular case of hot luminescence is associated with a radiative coherent emission.

Similar results have been obtained in pentaphosphate materials ($Nd_{0.75}La_{0.25}P_5O_{14}$), LiNdPO₃, and NdP₅O₁₄ in powder form (Gouedard et al. 1991, 1993). In all cases the R ion (Nd^{3+}) enters as a constituent of the host known to be of the weak self-quenching type (see sect. 3.2), that is, with lower ion–ion interaction.

One of the practical advantages of ASE and quasi-laser-like emissions of powders is that such an emission has been shown to be spatially incoherent while it is still temporally coherent (coherence time 8 ps); this is due to the macroscopic diffuse nature of the powder medium (Gouedard et al. 1993). Figure 14 shows streak camera spatio-temporal pictures of powder emission, and of a YAG:Nd laser for comparison. We clearly see temporal modulations of the emission that are due to the beating of modes: the spatial speckle pattern does not change with time. This stationary pattern is the signature of the temporal



Fig. 14. (a) Streak camera picture of the output far-field of a fiber fed by a multimode Nd:YAG coherent laser; (b) same as (a) but with the short emission of the hydrated neodymium chloride powder. Note the different time scale (from Gouedard et al. 1993).

coherence of the emission (fig. 14a); in fig. 14b the time-stationary speckle pattern is replaced by a temporal speckle pattern with a correlation time of the order of 10 ps. This is the signature of the temporal incoherence of the integrated emission.

In the case of lasers the spatial structure is regular whereas in the case of powders it is random. It has been anticipated that such sources may find applications whenever strong coherence is a drawback, such as in holography, transport of energy in fibers for medical applications, and master oscillators for fusion lasers.

2.2.3. The laser effect

Because the laser effect is a special case of ASE where feedback occurs, the necessary conditions on T_2 are the same as for ASE and are only given by eq. (108). This stringent condition is so weak that it is always fulfilled, and books about lasers do not even need to mention the existence of T_2 (Roess 1969, Weber 1979, Kaminskii 1981). It is so much the case that at room temperature, T_2 is reduced to a few tens of picoseconds by phonon interaction. On the other hand, because of the multifold nature of the laser cavity, τ_E is now the photon lifetime in the cavity, which is much larger than the travelling time in a distributed amplifier. It is given now by

$$\tau_{\rm E} = \frac{Q_{\rm c}}{2\pi\nu_0} = \frac{L}{c\gamma},\tag{112}$$

where L is the cavity length, C the speed of light in the laser medium, and γ the cavity losses due to the mirror's reflectivity (**R**). Because γ can be very small, τ_E being multiplied by γ^{-1} is usually very large, since $\gamma \approx 1-\mathbf{R}$ in case the losses are only due to the necessary cavity output mirror, and $\tau_E \gg T_2$. It is interesting to note at this point that the coherence between field and atom is not needed in a laser at the macroscopic scale; it exists only for individual atoms during the quasi-instantaneous interaction giving stimulated emission: in a laser, coherence is built macroscopically by the optical cavity in a statistical manner at times $\tau_E > T_2$. For this reason, although we have seen that spontaneous and stimulated emissions cannot be considered separately at time $t < T_2$, it is usual in laser theories (at $t > T_2$), to separate spontaneous and stimulated emission using, for example, a rate equation, or by adding 1 to the number of photon states n when spontaneous emission is introduced afterwards (Auzel 1992). This is the very method used initially by Einstein to introduce spontaneous emission through detailed balance and statistical considerations. Then one can understand why ASE and laser effects are much more easy to obtain than SR or SF and why they can exist at room temperature.

The condition for the laser effect is simply given by the threshold condition corresponding to the balance between gains and losses

$$aL = \gamma, \tag{113}$$

or

$$\Delta N_{\rm th} = \frac{1}{c\sigma_0\tau_{\rm E}} \ll \frac{1}{cT_2\sigma_0},\tag{114}$$

where σ_0 is the transition cross-section, and $\Delta N_{\rm th}$ the population inversion at threshold. Because a typical value for $(cT_2\sigma_0)^{-1}$ in an R system is ~10²¹ cm⁻³, which represents a very large value, the right part of eq. (114) is always fulfilled. In the general case the losses are also due to the laser material itself; one has to write:

$$\frac{1}{\tau_{\rm E}} = \frac{1}{\tau_{\rm L}} + \frac{1}{\tau_{\rm R}},\tag{115}$$

where τ_L^{-1} is the material contribution to the total losses and adds to the necessary output coupling loss τ_R^{-1} . When considering the R laser material as an optical-optical transducer, we are interested in knowing how much output power can be obtained for a given material under a given pumping flux in a cavity of known losses. Another way of presenting the threshold condition is to express it in terms of the volume density of cavity modes (p)in a spectral width $\Delta \bar{v}$

$$\Delta N_{\rm th} = p \frac{T_1}{\tau_{\rm E}},\tag{116}$$

with $p = 8\pi v_0^2/c^3 \Delta \bar{v}$ where the "statistical" Einstein relationship between spontaneous (A) and induced emissions (B) is used

$$T_{1}^{-1} = A = Bp \frac{h\nu_{0}}{\Delta \bar{\nu}},$$
(117)

which allows one to express σ_0 in terms of T_1 .

For practical purposes, using such a notation it is possible and convenient in a 4-level laser to give the pumping flux laser threshold as

$$\varphi_{\rm th} = p \frac{h \bar{\nu}_{\rm p}}{\tau_{\rm L}} \frac{(S+1)}{\sigma_{\rm p} \eta N_0},\tag{118}$$

where \bar{v}_p and σ_p are the pump frequency and cross-section, respectively; S is the cavity output coupling $(=\tau_L/\tau_R)$; η is the quantum efficiency for the laser transition which can be given as the ratio τ/T_1 where τ is the measured lifetime such that $\tau^{-1} = T_1^{-1} + W_{NR}$ (with W_{NR} the eventual non-radiative transition); N_0 is the volume of active R ion concentration.

With the same notation, the slope for the output power above the threshold (the laser "differential efficiency") is given

$$\frac{\Delta P_{\text{out}}}{\Delta \varphi_{\text{p}}} = \frac{S}{(S+1)} \frac{\nu_0}{\nu_{\text{p}}} \sigma_{\text{p}} N_0. \tag{119}$$

A good laser material parameter is the smallest possible threshold, obtained for S=0, that is, for a very weak output coupling. Then based on the denominator of eq. (118) a material Figure of Merit M can be defined as

$$M = \tau \sigma_{\rm p} \sigma_0 N_0. \tag{120}$$

How M can be optimized for R-doped materials in an engineering material way is the object of the next section.

3. Basic processes in R-doped materials for lasers

In the following, before describing how to optimize the quantum properties of a material for laser action, we shall present in simple ways the elementary knowledge of basic properties.

3.1. Radiative properties

3.1.1. Oscillator strengths and hypersensitive transitions

Phenomenological parameters such as lifetimes and cross-sections are linked to quantum mechanical microscopic properties of the doping ions by the so-called f-numbers. These are dimensionless numbers often used in spectroscopy to characterize the strength of a transition. They are pure numbers ≤ 1 . The f-numbers are linked to transition probabilities by:

$$A_{ij} = \frac{2e^2\omega_{ij}^2}{mC^3}n^2\chi f_{ij},$$
(121)

where χ is a local field correction valid for localized centers (Fowler et al. 1962, Auzel 1969b) in a medium of refractive index *n*:

$$\chi = \left(\frac{n^2 + 2}{3}\right) 2\frac{1}{n}.\tag{122}$$

A useful theoretical approach to oscillator strengths has been given by Judd (1962) who shows that electric dipole oscillator strengths for R ions can be given in terms of three parameters T_{λ} as

$$f = \frac{1}{\chi} \sum_{\lambda=2,4,6} T_{\lambda} \nu \left| \left\langle \Psi' J' \right| \left| U^{\lambda} \right| \left| \Psi J \right\rangle \right|^{2}, \qquad (123)$$

where the unit tensor reduced matrix element $\langle ||U^{\lambda}|| \rangle$ contains only orbital parts of the state wave functions, whereas T_{λ} contains the radial one and the odd crystal field part which promotes the parity forbidden 4f-4f electric dipole transitions.

Let us note that such is the case for most of the transitions in the ions considered because most of them take place within the same configuration, either 4f or 3d. By Laporte's Rule only magnetic dipole transitions are allowed in first order. Then electric dipole transitions shall depend on the host whereas magnetic dipole ones are host independent.

Knowledge of Judd's theory allows one to make some predictions as to the eventual changes in the transition probabilities when considering different hosts for a given ion. In particular, it is experimentally verified that T_2 is the parameter which is the most sensitive

to a large host modification. Then transitions for which intensity changes can be expected, are those for which $\langle ||U^2|| \rangle$ is not zero. Since:

$$\left\langle \psi SLJ \left| \left| U^{(\lambda)} \right| \right| \psi'S'L'J' \right\rangle = \delta(S,S')(-1)^{S+L'+J+\lambda} \times \left[(2J+1)(2J'+1) \right]^{1/2} \left\{ \frac{L\lambda L'}{J'SJ} \right\} \left\langle \psi SL \left| \left| U^{(\lambda)} \right| \right| \psi'S'L' \right\rangle,$$
(124)

one knows that one condition is to have the "6-j symbol" $\neq 0$

$$\begin{cases} L\lambda L' \\ J'SJ \end{cases} \neq 0 \quad \text{or} \quad \Delta J \leqslant 2,$$

which is the so-called triangle rule for J', λ , J. Other rules on are not significant because L is not a "good" quantum number. Then large changes for oscillator strengths can be expected only for transitions with $\Delta J \leq 2$; such transitions are called hypersensitive. "Pseudo-quadrupolar" transitions are advocated for the sensitivity of T_2 because the selection rule is of a quadrupolar type (Judd 1962) (this T_2 should not be confused with the T_2 lifetime defined in sect. 2.1.2).

3.1.2. Branching ratios and quantum efficiencies

Because T_{λ} was originally defined for ground-state absorption, it contains the *J*-number of the ground state; it is often useful to take out this dependence, writing

$$\Omega_{\lambda} = \frac{3h(2J+1)}{8\pi 2m\chi} T_{\lambda}.$$
(125)

Because T_{λ} contains the host information, once a set of three T_{λ} parameters has been obtained by absorption spectroscopy, it can be used to calculate probabilities for any other transition between excited states of the same ion (Auzel 1969b), provided U^{λ} matrix elements are known. Since these matrix elements involve free-ion states, they do not vary much from host to host and once calculated for one host they can be used expediently for others. Calculation of probabilities between excited states provides a convenient way to obtain the branching ratios (β) of transitions

$$\beta_{ij} = \frac{A_{ij}}{\sum_j A_{ij}},\tag{126}$$

which measures the percentage of emission for a given transition from a state (i) with respect to all other transitions from this state. By the same route, information on quantum efficiencies (η_i) can be reached. By definition we have for a level i

$$\eta_{i} = \frac{\tau_{i}}{T_{1i}} = \frac{\sum_{j} A_{ij}}{\sum_{j} A_{ij} + W_{\rm NR}},$$
(127)

where $W_{\rm NR}$ is the non-radiative probability for state *i* de-excitation.

We can define a quantum yield for one transition $i \rightarrow j$ by

$$\eta_{ij} = \frac{A_{ij}}{\sum_{j} A_{ij} + W_{\rm NR}} = \frac{\beta_{ij} \sum_{j} A_{ij}}{\sum_{j} A_{ij} + W_{\rm NR}} = \beta_{ij} \eta_i.$$
(128)

When $\beta_{ij} \neq 1$ for the laser emitting transition, then η_{ij} has to be introduced in the previous threshold calculation instead of η . Above threshold the branching ratio, as defined by eq. (128), loses its meaning because spontaneous emission is overstepped by stimulated emission.

3.2. Non-radiative transitions and vibronics

In this section we shall deal with multiphonon non-radiative and radiative processes. They can usually be considered in the first approximation as independent of the interactions between activator ions, that is, they are one-center processes. However in some peculiar cases they could also be concentration-dependent (Auzel 1980a).

Once an ion has been excited (in whatever way), it can lose energy non-radiatively by a transition from the excited level to that just below it. Experimentally it is found that the quantum efficiency of an excited state can be lower than would be expected from the one-phonon interaction for a given energy gap, even at low concentration (that is, without any possibility for energy transfer to sinks). A good description of this situation is given by the relation between the quantum yield of one level and the difference in energy with the next lower level. Monochromatic excitation has shown that energy decay effectively proceeds by cascade (Varsanyi 1964). The non-radiative transition probability (W_{NR}) can then be well described in terms of the energy difference ΔE between two consecutive levels, by an exponential law (Weber 1973)

$$W_{\rm NR}(\Delta E) = W_{\rm NR}(0)\exp - \alpha \Delta E, \qquad (129)$$

where (Miyakawa and Dexter 1971)

$$\alpha = \frac{1}{\hbar\omega_{\rm m}^{-1}} \left[\log_n \left(\frac{\bar{N}}{S_0(\bar{n}+1)^{-1}} \right) - 1 \right], \qquad \bar{N} = \frac{\Delta E}{\hbar\omega_{\rm m}}.$$

Here, ΔE is larger than $(\hbar \omega_m)$, the highest phonon energy of the matrix, which is the condition to be considered for a multiphonon process. Such exponential laws are found also for molecules and for deep centers in semiconductors. Except in a few cases where ΔE is of the order of the highest vibrational energy, no selection rule is found with respect to the set of quantum numbers of the levels.

Experimentally, $W_{\rm NR}$ is usually obtained through one of the three following methods:

(i) If W_{NR} is larger than W_R (the radiative transition probability), then a direct measurement of W_{NR} is obtained by a lifetime measurement for the level under consideration

$$W_{\rm NR} \approx 1/\tau.$$
 (130)





(ii) When W_{NR} is smaller than W_R , then W_R is first estimated from absorption measurement and W_{NR} is obtained by

$$W_{\rm NR} = 1/\tau - W_{\rm R}.$$
 (131)

(iii) Assuming the validity of the rate-equation model, one can solve the resulting system of equations for $W_{\rm NR}$ by measuring intensity ratios.

Equation (129) has been established by extensive simplifications of a statistical result (Auzel 1980a). This result can also be provided by two models: (i) the Nthorder perturbation method where electronic states are considered to be independent of the nucleus motion (Huang–Rhys parameter $S_0 \equiv 0$) (Kiel 1964); (ii) the nonadiabatic Hamiltonian method ($S_0 \neq 0$). This last method recognizes that in the Born–Oppenheimer approximation, the neglected term promotes the non-radiative transition. This approximation can be viewed as a configuration diagram (fig. 15) where the neglected term allows a mixture of the two electronic states, especially in the region where they are closer in energy. Two extreme cases can be considered: the electron-phonon coupling being strong $(S_0 > 5)$, or weak $(S_0 < 1)$. In the first case, in the Born–Oppenheimer approximation there can be a "level crossing" and non-radiative transitions can be viewed as a "short-circuit" between the two states. In the second case there is a tunneling of energy through the barrier between the two approaching states. This is what occurs in R ions, and then eq. (129) is a good approximation. Transition metal ions have S_0 values somewhere between these extremes, and it is safer to consider one of the equivalent full theories which have been reviewed and presented by Miyakawa and Dexter (1971), Fong (1975), Auzel (1978), Engelman (1979), Fong (1979), and Struck and Fonger (1991).

When states are not described by pure electronic wave functions but by Born-Oppenheimer states, then transitions of mixed-nature, partially vibrational and partially



Fig. 16. Energy scheme for radiative and non-radiative transitions in electron-phonon systems.

electronic (vibronics), are found in absorption, excitation, or emission. As for nonradiative transitions, vibronic transitions can be separated into two classes, according to the Huang-Rhys coupling parameter being zero or non-zero. This gives rise to the socalled M and Δ processes, respectively (Miyakawa 1973). For both non-radiative and radiative transitions, one deals with the coupling of an electronic state with a quasicontinuum (fig. 16), through an interaction which is either the nonadiabatic Hamiltonian or the electric-dipole operator.

The transition probability due to an interaction H can be expressed by the Fermi Golden Rule as

$$W_{21} = \frac{2\pi}{\hbar} \left| \left\langle 2 \left| H \right| \right\rangle 1 \right|^2 \rho, \tag{132}$$

where *H* is either the nonadiabatic Hamiltonian H_{NA} , or the electric-dipole operator eR; $|1\rangle$ and $|2\rangle$ are the two vibronic states between which the transition takes place; ρ is the density of the final states which can be expressed for a radiative transition as

$$\rho = R_{\rm N} \delta(E_2 - E_1 - E), \tag{133}$$

and for a non-radiative transition as

$$\rho = R_{\rm N} \delta(E_2 - E_1). \tag{134}$$

 R_N is usually given as a product of Franck–Condon factors corresponding to the so-called "accepting modes" which "receive" the energy released by the excited electronic state (Fong 1975). An estimation of R_N at 0K can be made by the following analysis (Auzel 1980a). Let p be the probability for one of a set of S equivalent modes to jump to the next state. p^N is the probability to have N simultaneous jumps in the same direction for

N modes. But the number of different ways to choose the N simultaneous jumping modes among the total set of S is

$$C_{\rm S}^{\rm N} = \frac{S(S-1)\cdots(S-N+1)}{N!}.$$

That is, the total probability p_t for N jumps among a set of S modes is

$$p_{t}^{(N)} = \frac{p^{N}S(S-1)\cdots(S-N+1)}{N!} \approx \frac{(pS)^{N}}{N!} \quad \text{for } S > N.$$
(135)

The term pS represents the average number of modes involved in the jump. Following Toyozawa (1967), S_0 (the Huang–Rhys coupling parameter, Huang and Rhys 1950), which is directly linked to the amount by which the normal coordinates are displaced by the electron–phonon coupling, can be viewed also as the number of phonons emitted or absorbed in the transition. It is then possible to write $pS = S_0$, and eq. (135) can be written as

$$p_{\rm t}^{(N)} = \frac{S_0^N}{N!}.\tag{136}$$

Now the total probability for all N-processes is equal to unity and we have

$$p_{\rm t} = \sum_{N} k \frac{S_0^N}{N!} = k e^{S_0} = 1,$$
 that is, $p(N) = \frac{e^{-S_0} S_0 N}{N!},$

a Poisson distribution sometimes called the "Pekarian" function. Now at temperature T, absorption and emission of phonons have to be simultaneously considered in such a way that

$$N=k-\ell,$$

• •

where k is the number of emitted phonons and ℓ the number of absorbed phonons. Then

$$p_{\ell}(N,T) = e^{-S_0(\bar{n}+1)} \frac{S_0^k(\bar{n}+1)^k}{k!} \frac{e^{-S_0} \bar{n} S_0^{\ell}(\bar{n})^{\ell}}{\ell!},$$
(137)

and in vibronic absorption for instance

$$p_{\ell}(N,T) = e^{-S_0(2\bar{n}+1)} \frac{(\bar{n}+1)^{N/2}}{(\bar{n})^{N/2}} \sum_{\ell} \frac{S_0^2 \bar{n}(\bar{n}+1)^{\ell+N/2}}{\ell!(N+\ell)!},$$
(138)

which is the R_N of Huang and Rhys (1950). If we consider eq. (138), as given by Huang and Rhys, the temperature dependence is complicated since it is contained in the phonon occupancy number,

$$\bar{n} = \left[\exp\left(\frac{\hbar\omega_{\rm m}}{kT}\right) - 1 \right]^{-1},$$

Type of transition	Type of active center	S ₀	
 f–f	rare earth (trivalent)	10 ⁻² -10 ⁻¹	
f-d	rare earth (bivalent)	16	
dd	transition metals	1.5–10	
	f-centers	10–120	

Table 1 Huang–Rhys electron–phonon coupling parameter (S_0) values for various active centers

$$R_{\rm N} = e^{-S_0} \frac{S_0^N}{N!} (\bar{n}+1)^N e^{-2\bar{n}S_0} \left(1 + \frac{S_0^2 \bar{n}(\bar{n}+1)}{(N+1)} + \cdots\right).$$
(139)

For $S_0 \leq 1$ (the R case) and not too high a temperature, we can limit eq. (139) to the first term; that is, we associate to a "Pekarian function" at 0 K a temperature dependence of the form

$$(\bar{n}+1)^N e^{-2\bar{n}S_0}.$$
 (140)

This factor gives the variation with temperature proposed by Fong et al. (1972). In fact, for small values of S_0 , the term $\exp -2S_0 \bar{n}$ can be neglected (it is ~4% for LaF₃ at 400 K) and one is left with the usual dependence as experimentally verified, for instance by Riseberg and Moos (1968). From this, the weak-coupling approximation of eq. (140) is equivalent, even at temperature T, only to phonon emission by $(\bar{n}+1)^N$, or absorption by $(\bar{n})^N$. This possibility arises from the rapid decrease of p(N) with the number of phonons. This is shown in fig. 17. According to the value of S_0 , and assuming that energy can be varied only by discrete equal steps for N (one phonon frequency), p(N) is represented as in fig. 17. For weak coupling ($S_0=0.1$), the envelope of the distribution is nearly exponential and represents the gap law we have seen (eq. 129). For medium ($S_0=1$) and strong ($S_0=10$) coupling the distribution becomes more symmetrical and approaches the usual Gaussian for such cases (Miyakawa and Dexter 1971).

Since this simple analysis (Auzel 1980a) underlying "Pekarian" functions can be applied to any phenomenon in which multiphonon jumps are involved, one can now understand why in the weak-coupling case one finds exponential gap laws for whatever process. For strong coupling the Gaussian form of p(N) gives the Arrhenius limit form for non-radiative probability (fig. 15). For weak coupling, N! is developed by Stirling's Formula, yielding eq. (129). Complete understanding of the phenomena enters when a modification to the statistics involved yields the gross features. Then such forms can be applied for non-radiative transitions as well as for radiative ones. The N=0 line is the so-called zero-phonon line, the intensity of which decreases with coupling strength. The electron-phonon coupling intensity depends essentially on the sensitivity of electrons in a given configuration to crystal field perturbation. Table 1 gives some typical orders of magnitude for S_0 , found for different configurations.

Although the involvement of a phonon side band in the laser effect is usually connected with the transition-metal tunable laser (Kaminskii 1981) because of the stronger S value

of the transition metal ions, such a phonon-terminated laser (Johnson et al. 1963) has also been demonstrated in R ions: Sm^{2+} (Vagin et al. 1968), and Ho^{3+} (Johnson and Guggenheim 1974). Use of a one-phonon cooperative process (see sect. 3.4.1) has been proposed to obtain an Yb^{3+} 4-level laser scheme (Dexpert-Ghys and Auzel 1984). Quite recently such a scheme has been found to be operative in apatite crystals (De Loach et al. 1994). When the concentration of active ions is increased, a migration of energy between the centers is found well before the appearance of new lines due to pairs or modifications in radiative transition probabilities. This is the subject of the following section, assuming that the multiphonon decay and the radiative transition remain one-center processes.

3.3. Energy transfers and up-conversion

Having discussed single-ion processes above, we shall deal now with multi-ion processes, namely energy transfers. Energy transfer occurs in a system when absorption and emission do not take place at the same center. It may occur without charge transport. One may distinguish between radiative and non-radiative, resonant and phonon-assisted energy transfer. Theoretical approaches start from a microscopic point of view with a macroscopic result averaged over all the centers in the sample. Figure 18 shows the different energy transfer processes. Although energy transfers in R have been reviewed in detail by Yen (1987), some points shall be recalled briefly for the sake of comprehensiveness and completeness.



Fig. 18. Different types of energy transfer to an activator ground state.

3.3.1. Energy transfer with the activator in its ground state

When the transfer is radiative, real photons are emitted by the sensitizer ions and are then absorbed by any activator ions within photon travel distance. As a result of this phenomenon, such a transfer depends on the shape of the sample. Moreover, according

to the degree of overlap between the emission spectrum of the sensitizer (S) and the absorption spectrum of the activator (A), the structure of the emission spectrum of the sensitizer will change with activator concentration. Since photons are emitted anyway, the sensitizer lifetime is independent of the activator concentration. These three facts are the criteria used to distinguish between radiative and non-radiative resonant energy transfer. The probability of such a transfer occurring between two ions at a sufficiently large distance R is found to be (Auzel 1980a)

$$p_{\rm SA}(R) = \frac{\sigma_{\rm A}}{4\pi R^2} \frac{1}{\tau_{\rm s}} \int g_{\rm S}(\nu) g_{\rm A}(\nu) \,\mathrm{d}\nu, \qquad (141)$$

where τ_s is the sensitizer lifetime and σ_A is the absorption integrated cross-section. The integral represents the spectral overlap between A and S. It should be noted that the distance dependence is R^{-2} . Such a resonant radiative transfer may permit long-range energy diffusion between identical ions and gives rise to photon-trapping effects of the same type as those observed in gases (Kuhn 1962). Trapping effects increase the apparent experimental lifetime and τ_s has to be measured on thin and lightly doped samples. These effects are particularly strong in Cr³⁺ and Yb³⁺ (Auzel 1969b, Auzel and Pécile 1973).

Let us consider the simple case of two ions, each with one excitable electronic state separated from its electronic ground state by nearly equal energy. With suitable interaction between the two electronic systems, the excitation will jump from one ion to the other before a quantum of fluorescence is emitted. The systems interact by Coulomb interactions of the Van der Waals type. Förster (1948), who first treated such a case by quantum-mechanical theory, considered the dipole-dipole interactions. He assumed that the interaction is strongest if, for both transitions, electric-dipole transitions are allowed (Förster 1960). The interaction energy (H_{SA}) is then proportional to the inverse of the third power of the interionic distance, and the transfer probability is given by

$$p_{\mathrm{SA}} = \frac{2\pi}{\hbar} \left| \left\langle S^* A^0 \left| H_{\mathrm{SA}} \right| S^0 A^* \right\rangle \right|^2 \rho_{\mathrm{E}},\tag{142}$$

where ρ_E is the density of states provided by the vibrational motion contributing to the linear broadening of the transition. The wavefunctions to be considered for the matrix element describe an initial state of the system with the sensitizer in its excited state and the activator in its ground state, the final state corresponding to the sensitizer in its ground state and the activator in its excited state. Therefore, the transfer probability can be written as

$$p_{\rm SA} = \frac{1}{\tau_{\rm s}} \left(\frac{R_0}{R}\right)^6,\tag{143}$$

where τ_s is the actual lifetime of the sensitizer excited state, including multiphonon radiative decay, and R_0 is the critical transfer distance for which excitation transfer and spontaneous deactivation of the sensitizer have equal probability.

However, Dexter (1953) pointed out that this theory should be extended to include higher multipole and exchange interactions. In fact, for an isolated atom one can consider the transition probability as decreasing as $(a_0/\lambda)^{2n}$, with a_0 the Bohr radius, λ the wavelength, and *n* an integer, whereas for an energy transfer process depending on near-zone interactions, the transition probabilities drop off as $(a_0/R)^{2n}$, with *R* the separation of the interacting ions. *R* can be as much as three orders of magnitude smaller than λ , so that the energy transfer effects tend to be more pronounced in systems with forbidden transitions (Dexter 1953). This holds true for ions with transitions forbidden to first order, such as transition metal and lanthanide ions. The energy transfer probability for electric multipolar interactions can be more generally written as (Dexter 1953)

$$p_{\rm SA} = \frac{(R_0/R)^S}{\tau_{\rm s}},\tag{144}$$

where S is a positive integer taking the following values:

- s = 6 for dipole-dipole interactions,
- s = 8 for dipole-quadrupole interactions,
- s = 10 for quadrupole-quadrupole interactions.

It should be noted that, for dipole–dipole interactions, the difference between radiative and non-radiative resonant transfers essentially lays in the following: for radiative transfers there is no critical R_0 depending only upon concentration. The variation is R^{-2} instead of R^{-6} , and the sensitizer lifetime does not depend on the distance R.

Equation (144) is not very useful for calculating $p_{SA}(R)$ effectively, because R_0 cannot be easily obtained theoretically. Applying Racah's tensorial methods at the beginning of the calculation, eq. (142) allows one to develop calculations analogous to Judd's theory for radiative transitions. The case of multipolar interactions was treated in this way by Kushida (1973), and generalization of the calculations to magnetostatic, and exchange interactions was performed by the CNET group (Pouradier and Auzel 1978). The general form for the energy transfer probability is obtained as

$$p_{\rm SA}(R) = \frac{2\pi}{\hbar} \frac{I}{g_{\rm S}^* g_{\rm A}^*} \sum_{\ell_1 \ell_2} \left| C \ell_1 \ell_2 \left\langle S^* \left| \left| U^{(\ell_1)} \right| \right| S^0 \right\rangle \left\langle A^0 \left| \left| U^{(\ell_2)} \right| \right| A^* \right\rangle \right|^2, \tag{145}$$

where $I = \int \gamma_{\rm S}(E) \Gamma_{\rm A}(E) dE$, $g_{\rm S}^*$ and $g_{\rm A}^*$ are the degeneracies of the S^* and A^0 levels, and $\gamma_{\rm S}(E)$ and $\Gamma_{\rm A}(E)$ are the normalized shape functions of the emission spectrum and the absorption spectrum, respectively. $U^{(\ell)}$ are the tensorial operators already seen for Judd's theory. $|C_{\ell_1\ell_2}|^2$ can be considered as a parameter analogous to T_{λ} for oscillator strength.

This expression of the transfer probability has three advantages: (i) radial and orbital parts have been separated; (ii) only a few reduced matrix elements need to be calculated (the same ones for the three interactions we consider, as long as interactions leave spins unchanged); (iii) comparison between two different interactions can be made through

comparison of $C_{\ell_1\ell_2}$ coefficients (they are independent of the states involved in the transfer and we call them $E_{\ell_1\ell_2}$, $M_{\ell_1\ell_2}$ and $X_{\ell_1\ell_2}$ for electrostatic, magnetostatic and exchange interactions, respectively).

Forced electric-dipole transitions are calculated by Judd's method, which can be included in eq. (145). This expression also gives a single mathematical form regardless of the type of interaction, which is a convenient result. [Somewhat complicated expressions for the different $C_{\ell_1\ell_2}$ of 4f electrons have been given by Pouradier and Auzel (1978)]. But we can note that for electrostatic interactions $E_{\ell_1\ell_2}$, the $\ell_1 = 1, \ell_2 = 1$ term, corresponding to dipole–dipole interaction, being zero in first order, necessitates the introduction of Judd's T_{λ} parameters. The $E_{\ell_1\ell_2}$ values are between $E_{22} \approx 30 \text{ cm}^{-1}$ for quadrupole–quadrupole intensities to $E_{66} \approx 3 \times^{-1} \text{ cm}^{-1}$, but all contain some dipole–dipole part due to the T_{λ} . For magnetostatic interactions $(M_{\ell_1\ell_2})$ only terms with $\ell_i = 1, 3, 5$, are nonzero, with the following order of magnitude: $M_{11} \approx 1 \text{ cm}^{-1}, M_{55} \approx 2 \times 10^{-7} \text{ cm}^{-1}$. For exchange interactions $(X_{\ell_1\ell_2})$ we have $1 \leq \ell_1 \leq 6$, giving estimates of $1-10^{-1} \text{ cm}^{-1}$ for the coefficients. These results show that exchange or magnetostatic interactions can be found in cases of small dipole–dipole and quadrupole electrostatic interactions if the matrix elements allow them.

When considering two ions with excited states of different energies, the probability for energy transfer should drop to zero where the overlap integral $\int g_{\rm S}(v)g_{\rm A}(v)dv$ vanishes. However, it is found experimentally that energy transfer can take place without phononbroadened electronic overlap, provided that the overall energy conservation is maintained by production or annihilation of phonons with energies approaching $k\Theta_d$, where Θ_d is the Debye temperature of the host matrix (Axe and Weller 1964). Then for a small energy mismatch (~100 cm⁻¹) energy transfer assisted by one or two phonons can take place (Orbach 1975). However, in energy transfer between rare earths, energy mismatches as high as several thousand reciprocal centimeters are encountered. This is much higher than the Debye cut-off frequency found in the usual hosts, so that multiphonon phenomena have to be taken into consideration here.

Miyakawa and Dexter (1971) showed that it is still legitimate to write the probability of energy transfer in the form of eq. (142), where $\rho(E)$ is taken as S_{SA} , the overlap of the lineshape functions for emission in ion S and absorption of ion A, including the phonon sidebands in the lineshape. It is necessary to consider each partial overlap between the *m*-phonon emission line shape of ion S and the *n*-phonon absorption lineshape of ion A. This mathematical assumption has gained experimental credibility through the existence of multiphonon sidebands for trivalent R ions which, in a case of very weak electronphonon coupling (Auzel 1976) could not be observed directly by usual spectroscopy.

Along the same lines as vibronic-sideband studies, S_{SA} can be expressed as follows

$$S_{SA} = \sum_{N} e^{-(S_{0S} + S_{0A})} \frac{(S_{0S} + S_{0A})^{N}}{N!} \alpha_{SA}(0, 0; E) \,\delta(N, \Delta E/\hbar\omega),$$
(146)

where S_{0S} and S_{0A} are the respective lattice coupling constants for the S and A ions; N is the order of the multiphonon process $(N = \Delta E/\hbar\omega_m)$; ΔE is the energy mismatch between both ions; $\hbar\omega_m$ is the phonon cut-off frequency; and $\alpha_{SA}(0,0;E)$ is the zerophonon overlap integral between S and A. For the same reason as explained in sect. 3.2, a "Pekar" function is still found.

The expression for S_{SA} with an energy mismatch of ΔE , for small S_0 constant, and for an occupation number $\bar{n} = [\exp(\hbar\omega/kt) - 1]^{-1}$ not exceeding unity at the operating temperature, can be approximated with Stirling's formula by

$$S_{\rm SA}(\Delta E) = S_{\rm SA}(0)e^{-\beta\Delta E},\tag{147}$$

where $S_{SA}(0)$ is the zero-phonon overlap between S and A. β is given by

$$\beta = (\hbar\omega)^{-1} \left[\frac{\log N}{S_0(\bar{n}+1)} \right] - \log\left(1 + \frac{S_{0A}}{S_{0S}}\right) \equiv \alpha_{\rm S} - \gamma \approx \alpha_{\rm S} - \log(2), \tag{148}$$

involving the non-radiative decay parameter α_s and assuming identical electron-phonon coupling for ions A and S. This exponential dependence on energy mismatch agrees well with experiment (Yamada et al. 1972).

Up to this point, we have been dealing with the microscopic case of two ions interacting with one another. In order to discuss the case of "real" macroscopic samples with many ions and to obtain a link with experimental facts, a statistical analysis of the energy transfer is necessary.

We have to consider the overlap integrals that, as we have seen, arise in all transfers between two ions. In the microscopic case, the lineshapes involved can only be due to some homogeneous broadening even for transfers between two identical ions at different lattice sites. In the macroscopic case, absorption and emission spectra take into account all broadening processes averaged over the whole sample, for instance the inhomogeneous broadening process due to emission and absorption at centers at different lattice sites. Then the overlap integral experimentally measured from the usual spectra is a measure in excess of the real overlap since we take into account emission and absorption of centers at any distances, even those which cannot interact. The error is largest for processes occurring at shortest interacting distance (exchange), and thus is certainly negligible for radiative transfer, since photons can travel a much larger distance than spatial disorder can spread. The error is smaller for systems with small inhomogeneous broadening, with centers at only one type of lattice site, that is, without disorder.

Fluorescence line-narrowing and coherent photon-echo techniques (Macfarlane 1992) could give some idea about the homogeneous part of an emission line, but the statistical analysis for the whole sample should still be performed. Supposing only a sensitizer-activator interaction, an average transfer efficiency can be calculated (Dexter 1953). This was studied in some detail by Inokuti and Hirayama (1965). They considered the number of activators located at random in a sphere around a sensitizer in such a way that the activator concentration remains constant when the volume of the sphere and the number

of considered activator ions are taken to infinity. Then the average probability for transfer from one sensitizer to any acceptor is

$$W_{\rm SA} = N_{\rm A} \int^{\infty} R_{\rm min} p_{\rm SA}(R) 4\pi R^2 \,\mathrm{d}R. \tag{149}$$

Introducing eq. (149) into the expression for the intensity emitted by all sensitizers, each experiencing a different activator neighborhood, they obtained the following relation for the intensity decay of the emission of the sensitizer surrounded by many activators,

$$I(t) = \exp\left[-\frac{t}{\tau_{s0}} - \Gamma\left(1 - \frac{3}{S}\right)\frac{C}{C_0}\left(\frac{t}{\tau_{s0}}\right)^{3/s}\right],\tag{150}$$

where τ_{s0} is the decay constant of the sensitizer in the absence of activators, *C* is the activator concentration, C_0 is the critical activator concentration, and *s* is the parameter of the multipolar interaction. The comparison between experimental decay and this theoretical expression has been widely used to determine the index of the multipolar interaction involved. This theory is valid only when there is no sensitizer–sensitizer or activator–activator transfer. This formulation, therefore, has to be modified for high sensitizer and activator concentrations. Then, in this case, rapid energy migration between sensitizers or between activators is possible, because of the perfect resonance conditions. The general result is complicated (Yokota and Tanimoto 1967) but, for large *t*, I(t) decays exponentially (Weber 1971),

$$I(t) = \exp\left(-\frac{t}{\tau_{\rm s}} - \frac{t}{\tau_{\rm D}}\right). \tag{151}$$

Two cases can then be distinguished:

(i) In one case, spontaneous decay of excited sensitizers, diffusion among sensitizers, and energy transfer between sensitizers and activators are of about the same order of magnitude. For sufficiently long times and dipole-dipole interactions, one has (Weber 1971)

$$\tau_{\rm D}^{-1} = V N_{\rm s} N_{\rm A},\tag{152}$$

where $V = 8\pi C^{1/4} C_{SS}^{3/4}$, N_S is the sensitizer concentration, N_A is the activator concentration, C is a sensitizer-activator energy transfer constant such as $C = (R_0)^{S/\tau}$, and C_{SS} is the sensitizer-sensitizer transfer constant.

(ii) For a high sensitizer concentration, the diffusion rate can be faster than spontaneous sensitizer decay or sensitizer-activator energy transfer. The limiting step is no longer diffusion and diffusion constant D appears to saturate with increasing donor concentration; each activator experiences the same excited sensitizer neighborhood. Taking for R the minimum distance between sensitizers as permitted by the lattice $(R=R_{min})$, we obtain

$$\tau_{\rm D}^{-1} = UN_{\rm A},\tag{153}$$

where U is a constant depending on the type of interaction as discussed earlier in this section (eq. 145). Another approach to the macroscopic case is the use of the well-known rate equations which deal with the population of ions in a given state. This



nearby identical ions Fig. 19. Two cross-relaxation processes: diffusion and quenching.

was used as a phenomenological approach in laser studies. The applicability of those equations in relation to the Inokuti–Hirayama statistics has been discussed by Grant (1958). Grants' basic result is that the energy transfer probability is proportional to the activator concentration,

$$W_{\rm t} = UN_{\rm A}.\tag{154}$$

This is the same result as obtained by fast-diffusion studies (eq. 153). The practical interest in considering diffusion is that the decays are again exponential, as when ions are not interacting. This validates the use of rate equations.

The cross-relaxation term usually refers to all types of energy transfer occurring between identical ions. In such a case, the same kind of ion is both a sensitizer and an activator. As shown in fig. 19, cross-relaxation may give rise to the diffusion process already considered between sensitizers, when the levels involved are identical, or to selfquenching when they are different. In the first case, there is a limited loss of energy, whereas in the second case there is a loss or a change in the energy of the emitted photons.

Theoretically we can use the same treatment as for the more general case of energy transfer; however, experimentally it may be more difficult to distinguish between sensitizers and activators. So any of the microscopic processes discussed above may happen with a maximum overlap when an identical couple of levels are involved. From the macroscopic point of view we have for the diffusion-limited case, from eq. (152):

$$\tau_{\rm D}^{-1} = V N^2 \qquad \text{for } N_{\rm S} = N_{\rm A} = N,$$
 (155)

and for the fast-diffusion case we have

$$\tau_{\rm D}^{-1} = UN.$$
 (156)

We shall illustrate these cases for Nd^{3+} laser materials below (sect. 4.1).

3.3.2. Up-conversion processes

When active ions are situated at a sufficiently short distance for interactions between them to take place, two types of up-conversion processes may occur: (i) summation of photons



Fig. 20. Energy transfers from a sensitizer (S) to an activator (A) in the ground state.



Fig. 21. Energy transfer with the activator in metastable excited states.

by energy transfers (Auzel 1966b), called the APTE effect (for Addition de Photon par Transferts d'Energie, Auzel 1973), or (ii) cooperative effects either by sensitization (Ovsyankin and Feofilov 1966), or emission (Nakazawa and Shionoya 1970). Both types are often mistaken one for the other because they present several similarities and may be simultaneously present in a given system for a given excitation.

Until 1966, all energy transfers between R ions were considered to be of the types summarized by fig. 20. That is, the activator ion receiving the energy from a nearby sensitizer (S), was in its ground state before interaction. Then it was proposed (Auzel 1966b) to consider cases where activators (A) were already in an excited state (fig. 21). Afterwards this became evident because one has to realize that we can exchange only energy differences between ions and not absolute energy.

The reason for proposing such an up-going transfer was that the type of energy transfer then used (Snitzer and Woodcock 1965) to improve the laser action of Er^{3+} , pumping Yb³⁺ in a glass matrix, could also have the detrimental effect of increasing reabsorption (Auzel 1966b, 1969a). A simple proof of this effect was the observation of



Fig. 22. Energy schemes for different 2-photon up-conversion processes with quantum efficiency in cm²/W for specified materials (Auzel 1990).

an up-converted green emission (from ${}^{4}S_{3/2}$ of Er^{3+}) while pumping Yb^{3+} (${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$) (Auzel 1966b, Auzel and Deutschbein 1969). Of course, the situation in fig. 21 could repeat itself several times at the activator. This means that *n*-photon up-conversion by energy transfer is possible as demonstrated by the 3-photon up-conversion of 0.97 μ m into blue light (0.475 μ m) in the Yb³⁺-Tm³⁺ couple (Auzel 1966b). Such IR \rightarrow blue up-conversion was interpreted independently by Ovsyankin and Feofilov (1966) as a 2-photon effect connected with a cooperative sensitization of Tm³⁺ by two Yb³⁺ ions, because of saturation in an intermediate step reducing the intensity from a cubic to a quadratic law.

In order to clarify the terminology, fig. 22 presents a schematic comparison between the APTE effect and other 2-photon up-conversion processes, namely: 2-step absorption, cooperative sensitization, cooperative luminescence, second-harmonic generation (SHG), and 2-photon absorption excitation; typical efficiencies are also given there. Since we are dealing with nonlinear processes, the usual efficiency, defined in percentage, has no meaning because it depends linearly on excitation intensity. Values are then normalized for incident flux and given in units of cm^2 W. A simple inspection of the energy schemes involved shows that at first sight they differ by the resonances involved for in- and outgoing photons: for the highest efficiency, photons have to interact with the medium a longer time, which is practically obtained by the existence of resonances. As shown, the APTE effect is the most efficient because it is the process which nearest approaches the full resonance case; consequently it is the more likely to be encountered.

However, reality is not that simple and different up-conversion processes may exist simultaneously, or their effects can be tentatively reinforced reciprocally. For instance, two-photon absorption and cooperative absorption have been theoretically investigated (Rios Leite and de Araujo 1980). Also SHG and cooperative luminescence have been considered simultaneously, in order to increase SHG by the partial resonance of cooperative luminescence (Bonneville and Auzel 1976, Ovsyankin and Fedorov 1981).

In the literature, up-conversion involving coupled ions is often referred to as cooperative effects without proof (Van der Ziel et al. 1986, Kintz et al. 1987, Desurvire

1994) while, as can be guessed from their relative efficiencies, APTE effects are in fact involved (Auzel 1984a, Auzel et al. 1989a). The fact that the APTE effect and cooperative effects are often mistaken is caused by a number of properties they have in common. For instance, for 2-photon up-conversion, both processes show a quadratic increase on excitation and on absorber concentrations; both show an emission lifetime equal to half the absorber lifetime. However, as shown below, the difference is more basic, though sometimes difficult to establish experimentally, except in special cases: when single-ion resonances clearly do not exist, or when diffusion between ions is prohibited by too small a concentration while there still is interaction, as in clusters of R ions.

3.3.2.1. Up-conversion in single-ion-level description (APTE) and in pair-level description (cooperative effects). As seen in the introduction, up-conversion by energy transfer is just the generalization of Dexter energy transfer (Dexter 1953) to the case of the activator being in a metastable state instead of being in its ground state; this requires the interaction between S and A (H_{SA}) to be smaller than the vibronic interaction between S and A (H_{SA}) to be described by single-ion levels coupled to the lattice. This is generally the case since for fully concentrated R crystals or for clusters, pair-level splitting is of the order of 0.5 cm^{-1} (Ovsyankin 1987); in a host with a smaller concentration this interaction can even be weaker, whereas one-phonon or multiphonon sidebands may modulate the level positions by several 100 cm⁻¹. In addition, up-conversion requires that the transfer probability for the second step W_{SA} be faster than radiative and non-radiative decay from the metastable level, that is, $W_{SA} > \tau^{-1}$ with τ the measured lifetime. W_{SA} is obtained from

$$W_{\rm SA} = \frac{2\pi}{\hbar} \left| \left\langle \Psi_{\rm S}^{\rm e} \Psi_{\rm A}^{\rm 0} \left| H_{\rm SA} \right| \Psi_{\rm S}^{\rm 0} \Psi_{\rm A}^{\rm e} \right\rangle \right|^2 \rho(E), \tag{157}$$

where the wave functions are simple products of single-ion wave functions; $\rho(E)$ describes the dissipative density of states due to the coupling with the lattice.

On the other hand, all cooperative processes including up-conversion can be considered as transitions between a pair level for both ions as a whole. A dipolar electric transition would be forbidden for such a two-center transition and one needs product wave functions corrected to first order to account for the interaction between electrons of different centers (Stavola and Dexter 1979):

$$\Psi_{\text{pair}} = \Psi^{0}(S)\Psi^{0}(A) - \sum_{s''\neq 0} \sum_{a\neq 0} \frac{\langle s''a'' | H_{SA} | 00 \rangle}{\delta_{s''} - 0 + \varepsilon_{a''} - 0} \Psi_{s''}(S)\Psi_{a''}(A),$$
(158)

for example for the ground state; here s'' and a'' denote intermediate states for S and A, $\delta_{s''}$ and $\varepsilon_{a''}$ denote their corresponding energies. Then any one-photon transition in the cooperative description already involves four terms in the matrix element which cannot be reduced to eq. (157).

APTE up-conversion does not correspond to the same order of approximation as cooperative processes; in practice the latter have to be considered only when APTE cannot take place. This is the case when real levels do not exist to allow energy transfers, like $Yb^{3+}-Tb^{3+}$ up-conversion (Ovsyankin 1987), or when concentration is to small to allow efficient transfer by energy diffusion between sensitizers. Then cooperative up-conversion is likely to occur within clusters (Vial et al. 1979, Auzel et al. 1994a). One may also look for crystal structures where pair clustering is built in (Cockroft et al. 1989, Pellé and Goldner 1993).

In order to illustrate the difference between APTE and cooperative up-conversion, we shall discuss an example of a line-narrowing effect in *n*-photon summation as a means to distinguish between both processes (Auzel 1984a, 1985). Irradiating Er^{3+} -doped samples with IR photons at 1.5 µm leads to various visible emissions. Room-temperature IR F-center laser excitation between 1.4 and 1.6 µm of 10% Er^{3+} -doped vitroceramic and of Er^{3+} :YF₃ leads to emission bands from near IR to UV. Such emissions may be ascribed to multiphoton excitation of the order of 1 to 5, either by APTE or by the cooperative type, with energy levels of single ions (APTE), or with pair levels, respectively, as illustrated by fig. 23. Successive absorptions in fig. 23a involve a combination of several J states. The APTE effect, because of self matching by multiphonon processes, involves only $J = \frac{15}{2}$ and $J = \frac{13}{2}$ states.



Fig. 23. *n*-photon summation (n=1, ..., 5) in Er^{3+} system by (a) cooperative sequential pair absorption, and (b) APTE effect (Auzel 1984a).



Fig. 24. Excitation spectra for *n*-photon summation in YF_3 : EF^{3+} (Auzel 1985).

The excitation spectra depicted in fig. 24 show a striking behavior: each spectrum presents the same spectral structure, but an increasing narrowing is clearly observed with process order. The structure reproduces the Stark structure of the ${}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$ first excited terms as can be obtained by a diffuse reflectance spectrum. This then is a direct proof of the validity of the APTE explanation, since a cooperative effect should show the convolution of all *J* states involved in the multiple absorption between pair-levels (Auzel 1985). The spectral narrowing can be understood by a rate-equation treatment where a higher excited population is neglected with respect to the lower ones in order to obtain a tractable development (weak excitation assumption). The emitted power from an *n*-photon summation is then given by:

$$P_n(\lambda) = \frac{W_n \cdots W_2}{(\omega_{(n-1)} \cdots \omega_2)} P_1^n(\lambda), \tag{159}$$

with the symbols of fig. 23, and with $P_1(\lambda)$ the line shape of the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ absorption (Auzel 1984a).

3.3.2.2. ESA and the APTE effect. The probability for Excited State Absorption (ESA) in a two-step absorption (W_{13}) , connecting a state E_1 to E_3 by the intermediate state E_2 , is just given by the product of the probabilities for each step

$$W_{13} = W_{12} \cdot W_{23}. \tag{160}$$

For ESA by the APTE effect we have also the product of two energy transfers probabilities. Calculating the rate for the same ESA transition with APTE, it follows

$$N_{\rm A}W_{13} = (N_{\rm A}N_{\rm A}^*W_{\rm SA1})N_{\rm S}^*W_{\rm SA2},\tag{161}$$

or

$$W_{13} = N_{\rm S}^{*2} W_{\rm SA1} W_{\rm SA2},\tag{162}$$

where W_{SAi} are the energy transfer probabilities for each step *i*, and N_S^* is the concentration of excited sensitizers, given by

$$N_{\rm S}^* = N_{\rm S} W_{12}$$
.

Assuming all W_{ij} and W_{SA} to have the same magnitude, as is typical for R ions, we have to compare

$$W_{13} = W_{12}^2 \qquad \text{single-ion ESA,} \tag{163}$$

$$W_{13} = W_{12}^2 N_3^2 W_{SA}^2$$
 ESA by APTE. (164)

Clearly the gain by APTE over one-ion ESA can come from the product $N_S^2 W_{SA}^2$ which has to be > 1. This points to an increase in sensitizer concentration (N_S) which is known to lead to "fast diffusion" (Auzel 1992), and allows the use of rate equations in such multi-ion systems (Auzel 1987) (see sect. 3.3.1).

3.3.2.3. *Photon avalanche effect.* In experiments looking for 2-step ESA in Pr^{3+} -doped LaCl₃ and LaBr₃ at low temperature (< 40 K) as a means to detect an IR photon by its energy summation with a more energetic photon performing ESA, it was found that the higher energy photon alone could, simultaneously, give rise to up-conversion and reduce the transmission of the sample above a given intensity threshold (Kueny et al. 1989) (see fig. 25). The effect was attributed to an increase of population in an excited state resulting from a cross-relaxation process.

The starting process was initially not completely determined. In the Pr^{3+} case, the ${}^{3}H_{5} \rightarrow {}^{3}P_{1}$ absorption is initially very weak at low temperature because ${}^{3}H_{5}$ is about 2000 cm⁻¹ above ground state (see fig. 26), however, above about 1 mW of excitation this transition is increased; the cross-relaxation (${}^{3}H_{6}, {}^{3}H_{4}$) \rightarrow (${}^{3}H_{5}, {}^{3}H_{5}$) increases the ${}^{3}H_{5}$ population, which in turn reduces the transparency of the sample at the (${}^{3}P_{1}-{}^{3}H_{5}$) energy. Since the more (${}^{3}P_{1}-{}^{3}H_{5}$) energy is absorbed, the more the ${}^{3}H_{5}$ population is increased, the process was termed "photon avalanche" (Kueny et al. 1989, Case et al. 1990). It is clearly a way to increase ESA in a sample.

Later, similar effects have been observed in Sm³⁺, Nd³⁺, Ni²⁺, Tm³⁺-doped halide crystals (Krasutsky 1983, Lenth and Macfarlane 1990, Oetliker et al. 1992, Ni and Rand 1991). The distinct features of the photon avalanche process are nonlinear dependences



Fig. 25. Decrease of transmission in a Pr^{3+} :LaCl₃ sample under ${}^{3}H_{5}-{}^{3}P_{1}$ energy pumping (after Kueny et al. 1989).

Fig. 26. Energy levels involved in the avalanche process of Pr^{3+} (Kueny et al. 1989).

of (i) transmission, (ii) emission, and (iii) rise time of the pump power intensity with the existence of a critical pump threshold. Particularly long rise times from seconds to minutes have been observed (Pelletier-Allard and Pelletier 1987).

Recently, some of the features of the avalanche effect have been observed at room temperature in Tm^{3+} :YAlO₃ (Ni and Rand 1992), and in Pr^{3+} in silica glass fibers (Gomes



Fig. 27. (a) Transition involved in avalanche emission of $\text{LiYF}_4:\text{Er}^{3+}$, with cross-relaxations indicated by solid circles; (b) electronic and multiphonon absorption bands for $\text{LiYF}_4:\text{Er}^{3+}$, heavy lines show room-temperature anti-Stokes excitation spectral region for the avalanche (Auzel and Chen 1995).

et al. 1993); however, up until now, only Er^{3+} has shown, at room temperature, all the above features of an avalanche in a ZBLAN fluoride glass both in bulk and in a fiber shape; even the long delay of several seconds to minutes was observed (Auzel et al. 1994b, Chen and Auzel 1994a,b, Auzel and Chen 1995). In the case of Er^{3+} , the first step for photon avalanche has been clearly identified and attributed to anti-Stokes multiphonon sidebands absorption (Auzel et al. 1994b) (see fig. 27).

In fluoride fiber there appear as yet not completely explained up-conversion spatial domains with periodic structure, with periods ranging from few cm to mm and 100 μ m (Chen and Auzel 1994a,b). Such avalanche effects have been found to be a way to obtain population inversions and consequently ESA and laser effects (Koch et al. 1990, Lenth and Macfarlane 1990, Hebert et al. 1992, Chen and Auzel 1994c).

4. Engineering approach to R materials for lasers

The first condition for a laser material is to show a threshold. Experimentally of course a threshold exists only after it has been reached; this makes laser experiments with new materials frustrating at times. The best material shall then be the one with the lowest threshold. Based on eq. (118), the condition is to have the Figure of Merit M as large as possible,

$$M = \tau \sigma_{\rm p} \sigma_0 N_0; \tag{165}$$

this parameter contains all dependencies on the quantum properties of the materials. The loss parameter $\tau_{\rm L}$ is not taken into account since it strongly depends on the quality of the technology used for growing the material. At any rate, $\tau_{\rm L}$ has to be as large as possible. The Figure of Merit is a product of parameters discussed in the above sections, which are either concentration independent (one-center process), like $\sigma_{\rm p}$ and $\sigma_{\rm 0}$, or concentration dependent (multicenter process), like τ which should be written $\tau(N_0)$ because of the concentration self-quenching phenomena. Self-quenching is usually caused by cross-relaxation (sect. 3.3.1) and is characterized by a reduction of τ , and consequently of η , with increasing concentration. This effect has to be compromised with the factor N_0 appearing also in M.

In addition to threshold, slope efficiency is important in a laser. Equation (119) shows that high $\sigma_p N_0$ also increases the slope for a given output coupling. We are left with the highest output coupling adapted to internal losses and to pumping level (Di Bartolo 1968)

$$S_{\text{opt}} = -1 + \left(\frac{\Phi_{\text{p}}}{[\Phi_{\text{th}}]R_{\text{max}}}\right)^{1/2}.$$
(166)

For a given pumping level above threshold, S_{opt} will be larger the smaller $[\Phi_{th}]R_{max}$ is; which is the threshold for a cavity without output coupling. Then the Figure of Merit optimizes also the differential slope efficiency of the laser, provided the laser frequency is near the pumping one. The efficiency Figure of Merit can be found from eqs. (119) and (165) (Auzel 1987)

$$M_{\rm e} = M^{1/2} \frac{v}{v_{\rm p}} \sigma_{\rm p} N_0 = \frac{v}{v_{\rm p}} \tau^{1/2} \sigma_0^{1/2} \sigma_{\rm p}^{3/2} N_0^{3/2}, \quad \text{assuming } S < 1.$$
(167)

The factor $N_0^{3/2}$ shows the important role of concentration in 4-level lasers.

In the following we present a number of short-cuts for the investigation of new ionic laser materials (Auzel 1987). Such methods are based upon the previous background (see sect. 3), but favor approximations over completeness in order to reduce investigation time and expenses for material preparation.

4.1. Materials for CW lasers

4.1.1. Powdered samples luminescence as an approach to Figure of Merit (global optimization of M)

When relative intensity emission of fluorescence versus active ion concentration is studied, a typical bell-shaped curve is obtained as illustrated in fig. 28. At lower



Fig. 28. Fluorescence intensity versus N_0 for typical and weak self-quenching materials (Auzel 1980c).

concentration, intensity increases with concentration because more excitation energy is absorbed up to the point where concentration quenching counter-balances this increase. Usually, at higher concentration, self-quenching dominates which explains the drop in intensity.

Let us find out what information can be obtained from such a result in correlation with laser properties. Energy efficiency for fluorescence is defined as

$$\eta_{\text{energy}} = \frac{I_{\text{f}}}{I_{\text{a}}} \approx \frac{I_{\text{f}}}{I_i \sigma_{\text{p}} N_0 \ell},\tag{168}$$

where I_f is the fluorescence intensity, I_a is the absorbed excitation intensity, I_i is the incident excitation intensity, and ℓ is the optical path for uniform absorption (thin layer).

Since

$$\eta_{\text{energy}} = \eta \frac{\nu}{\nu_{\text{p}}},\tag{169}$$

we have

$$I_{\rm f} = \frac{\tau}{T_1} \frac{\nu}{\nu_{\rm p}} \sigma_{\rm p} N_0 \ell I_{\rm i},\tag{170}$$

-		-	-		-
Material	$C_{\rm Nd}~({\rm cm}^{-3})$	$I_{\rm fmax}$ (relative to NdUP) (grain di- ameter $\approx 100\mu{\rm m}$)	$\Delta v_{\rm eff}~({ m cm}^{-1})$	Figure of Merit (relative to NdUP)	Quenching rate ^a Q (s ⁻¹)
NdP ₅ O ₁₄ (NdUP)	3.9×10 ²¹	100	127	1	2.7
Na ₂ Nd ₂ Pb ₆ (PO ₄)Cl ₂ (CLAP)	3.4×10 ²¹	120	134	1.1	1.8
NdTa7O19	3.1×10 ²¹	50	110	0.6	2.2
$Na_5Nd(WO_4)_4$	2.6×10 ²¹	230	125	2.4	2.4
NdAl ₃ (BO ₃) ₄ (NAB)	5.4×10 ²¹	70	72	1.3	2.5
$KNdP_4O_{12}$ (KNP)	4.1×10 ²¹	190	131	1.8	2.8
LiNdP ₄ O ₁₂ (LNP)	4.4×10 ²¹	190	85	2.9	2.4
YAG:1%Nd	1.4×10 ²⁰	80	68	1.5	>20

 Table 2

 Relative Figure of Merit for different low self-quenching Nd³⁺ self-activated materials in powder form

^a $Q = \tau_{high}^{-1} - \tau_{low}^{-1}$. τ_{high} : $C_{Nd} > 10^{19} \text{ cm}^{-3}$; τ_{low} : $C_{Nd} < 10^{19} \text{ cm}^{-3}$.

which using eq. (118) becomes

$$I_{\rm f} = \sigma_0 \sigma_{\rm p} \tau N_0 \left(\frac{8\pi v^2}{c^2} \Delta \bar{v} \frac{g_1}{g_2} \frac{v}{v_{\rm p}} \right) \ell I_{\rm i}; \tag{171}$$

then

$$\frac{I_{\rm f}}{\Delta \bar{v}} = M \times (\text{constant for ion and excitation geometry}),$$

and this can be considered as a relative Figure of Merit for the laser.

 $I_{\rm f}$ is measured in a reproducible way by a well defined geometry and $\Delta^{-}v$ is obtained from the emission spectrum by

$$\Delta \bar{\boldsymbol{\nu}} = \frac{\int I_{\rm f}(\boldsymbol{\nu}) \, \mathrm{d}\boldsymbol{\nu}}{I_{\rm fmax}}.$$
(172)

Such a "powder method" was proposed and usefully applied (Auzel 1980c) as a fast first investigation method for the research of high-concentration Nd³⁺ laser materials. In such research the purpose was to find materials with small self-quenching, thus allowing high doping concentration, up to 100% where the active ion becomes a matrix constituent (Budin et al. 1979). Examples of such research are presented in table 2. The best relative Figure of Merit is obtained for LiNdP₄O₁₂, the so-called LNP material, with a relative M twice as good as 1%-doped YAG. Besides consideration of M, the small self-quenching of LNP, defined by the ratio of τ at $N_0 \leq 10^{19}$ cm⁻³ and τ at $N_0 = 10^{21}$ cm⁻³, or by the concentration at which τ is reduced to $\frac{1}{2}\tau$, allows realization of very small laser lengths with L of the order of a few tens of microns. YAG has

been used for comparison; however because of the much stronger self-quenching, only a 30 times smaller concentration is used, hence the effective optical path is very different from other powder materials; this makes the relative Figure of Merit for YAG less meaningful, as shall be seen by comparing it with the absolute values of M. A refinement would be to use Melamed's theory (Melamed 1963) for powder emission, taking into account multiple diffusion and total refraction at grain boundaries, but this would ruin the simplicity of the method. The method is then essentially valid for a first approach and for materials which are planned to be used under the same laser conditions. By this token table 2 refers to high-concentration, small-dimension laser materials.

Besides having the rapid and global methods described above for optimization before the crystal growth process, attempts have been made at a more predictive approach (Auzel 1979) which should be useful for the materials research of compact lasers of the "stoichiometric minilaser" type (Danielmeyer and Weber 1972) (see sect. 6), or of the "microchip" type (Zayhowski and Mooradian 1989).

4.1.2. Self-quenching and crystal field strength (optimization of the product τN_0)

Besides a number of effects leading to self-quenching, such as the crystal-field orbital mixing, exciton annihilation, up-conversion recombination, concentration-enhanced electron-phonon coupling, reviewed by Auzel (1980a), the basic effects are often crossrelaxation or energy diffusion to sinks. When it is desired to increase the energy density inside a laser material, the active ion density has to be increased. Unfortunately however, for any luminescent system, a high activator concentration generally leads to poor quantum efficiencies for emissions. This is the pervading effect of self-quenching usually due to the combination of two types of energy transfer between identical activators: resonant diffusion through identical pairs of levels or transfer to unwanted impurities. Figure 29 illustrates the energy scheme for such processes in Nd³⁺. In some cases materials with rather small self-quenching may be found such as the so-called stoichiometric laser materials: NdP₅O₁₄ (NdUP or NDPP) is the archetype of such materials (Danielmeyer and Weber 1972), where the active ion is a matrix constituent. This effect can be characterized by defining a quenching rate

$$R_{\rm Q} = \frac{1}{\tau} - \frac{1}{\tau_0},\tag{173}$$

where τ_0 is the radiative lifetime (T_1) , and τ is the measured lifetime at high activator concentration $(10^{21} \text{ cm}^{-3} \text{ for } \text{Ln}^{3+})$.

Other processes produce only moderate effects for Nd^{3+} and cannot explain why in some materials concentration quenching is important even at ~ 10^{20} cm⁻³, (e.g., YAG, $R_Q \approx 10^5$ s⁻¹) whereas in some other materials it is not (e.g., NdPP, $R_Q \approx 5 \times 10^3$ s⁻¹). The strong self-quenching of Nd³⁺ in Na_{0.5}Gd_{0.5}WO₄:Nd (Peterson and Bridenbaugh 1964), LaF₃:Nd (Asawa and Robinson 1966), YAG:Nd (Danielmeyer 1975), or glass


Fig. 29. Diffusion and self-quenching by cross-relaxation in Nd^{3+} ions.

(Chrysochoos 1974), has been known for a long time to be due to the following crossrelaxation energy transfer

$$Nd_{A}^{3+}({}^{4}F_{3/2}) + Nd_{B}^{3+}({}^{4}I_{9/2}) \to 2Nd^{3+}({}^{4}I_{15/2}),$$
(174)

as depicted in fig. 29. Such a transfer is rather of the non-radiative resonant type (see sect. 3.3.1). When energy-matching for resonance is insufficient, phonon-assisted energy transfer may take place in addition to eq. (174), according to

$$Nd_{A}^{3+}({}^{4}F_{3/2}) + Nd_{B}^{3+}({}^{4}I_{9/2}) \to 2Nd^{3+}({}^{4}I_{13/2}) + N_{1}\hbar\omega_{m},$$
(175)

or

$$Nd_{A}^{3+}({}^{4}F_{3/2}) + Nd_{B}^{3+}({}^{4}I_{9/2}) \to Nd_{A}^{3+}({}^{4}I_{13/2}) + Nd_{B}^{3+}({}^{4}I_{15/2}) + N_{2}\hbar\omega_{m}.$$
 (176)

Of course, at high concentration, energy migration is also involved and one can view cross-relaxation as an exciton annihilation process. Because of the rapid multiphonon non-radiative relaxation between levels above ${}^{4}F_{3/2}$, the most likely energy path for diffusion is

$$Nd_{A}^{3+}({}^{4}F_{3/2}) + Nd_{B}^{3+}({}^{4}I_{9/2}) \to Nd_{A}^{3+}({}^{4}I_{9/2}) + Nd_{B}^{3+}({}^{4}I_{3/2}),$$
(177)

Since transition probabilities involved in the above relations for resonant transfer are not expected to vary too much from matrix to matrix (Auzel and Michel 1975), the role played by the overlap integral should be most important in comparing strong- and weak-quenching materials. This results directly from eq. (145) in sect. 3.3.1. Table 3 presents some results showing effectively that measured overlap integrals (${}^{4}F_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$) are systematically smaller for weak-quenching materials.

On the other hand, the overlap for the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ diffusion transition is much larger and about constant. From this it was inferred (Auzel 1979) that weak-quenching

Maximum concentration $(10^{21} \text{ cm}^{-3})$	Quenching at maximum concentration R_Q (10 ³ s ⁻¹)	Cross-relaxation overlap (10 ⁻⁴ Kayser ⁻¹)		
		Quenching	Diffusion	
5.45	240	6.5	15	
0.8	100	4	15.7	
3.96	5.2	0.65	11.6	
3.4	6	1.4	18.3	
	5.45 0.8 3.96 3.4	Analytical maximum (10^{21} cm ⁻³) Questioning at maximum concentration R_Q (10^3 s ⁻¹) 5.45 240 0.8 100 3.96 5.2 3.4 6	Internation Questioning Cross relation over the concentration over the concentration over the concentration R_Q (10 ³ s ⁻¹) Quenching 5.45 240 6.5 0.8 100 4 3.96 5.2 0.65 3.4 6 1.4	

Table 3 Nd³⁺ spectral overlap integral for diffusion $({}^{4}F_{3/2}, {}^{4}I_{9/2})$ and quenching $({}^{4}I_{13/2}, {}^{4}I_{15/2}, 4I_{9/2})$ of strong and weak self-quenching materials

or strong-quenching materials behave in a way predicted by known energy-transfer processes without resorting to new ones. In the case of NdLaPP and other weak-quenching materials, the quenching rate R_0 is found to be given by (see fig. 30)

$$R_{\rm O} = kN,\tag{178}$$

where N is the Nd³⁺ concentration. This is the same form as eq. (156) for the "fastdiffusion case". In the case of YAG, glasses, and strong-quenching materials, quenching is found to be (fig. 30)

$$R_{\rm Q} = kN^2 \tag{179}$$

which is the form of eq. (155) for the diffusion-limited case. Such a form has also been found for NdPP (Strek et al. 1977). This discrepancy can be linked to the following result: for $K_3Nd(PO_4)_2(KNP)$, at concentration 3.2×10^{20} cm⁻³, a quadratic dependence on N is found, whereas for $N = 3.2 \times 10^{20}$ cm⁻³ a linear behavior with N predominates (Hong and Chinn 1976). This may be ascribed to a passage from limited to fast diffusion with increasing concentration (Kaminskii 1978). Also, as seen in sect. 3.3.1, the distinction between the two regimes for fixed concentration is in relation to the strength of the crossrelaxation energy transfer with respect to the diffusion one: a strong quenching overlap would give "limited diffusion", whereas a small overlap would give "fast diffusion". But for a particular crystal, if the relative probabilities for diffusion and quenching are modified for whatever reason, one could expect a change in the expected diffusion behavior. The results of table 3 for overlaps are in good agreement with the concentration power law behavior of fig. 30.

At any rate, the linear or the square law does not reflect the type of interaction, although this argument is sometimes found in the literature to reject or assume cross-relaxation, dipole–dipole, or exchange interaction. The observed laws are only of a statistical origin, the type of interaction gives the magnitude of the constant. For the same reason, the F. AUZEL



Fig. 30. Self-quenching rate for high- and low-quenching materials. Points for YAG and NdPP taken from Kaminskii (1978).

Table 4 Comparison of the self-quenching rate R_Q of Nd³⁺ (⁴F_{3/2}) and Tb³⁺ (⁵D₃) at $N = 4 \times 10^{21}$ cm⁻³ in two stoichiometric materials

Material	d_{\min} (Å)	Nd ³⁺ (⁴	$F_{3/2}$)	$Tb^{3+}({}^{5}D_{3})$	
	$(Ln^{3+}-Ln^{3+})$	$R_{\rm Q} \ (10^4 {\rm s}^{-1})$	Slope	$R_{\rm Q} \ (10^4 {\rm s}^{-1})$	Slope
NaLn(WO ₄) ₂	3.9	30	2	4	1
LnP5O14	5.2	0.5	1	13	2

shortest distance between ions, though often claimed, does not seem to be the most important parameter. Proof is given by the results reported in the following section. Comparing, for example, the behavior of $Nd^{3+}({}^{4}F_{3/2})$ and $Tb^{3+}({}^{5}D_{3})$ in table 4, it was demonstrated (Auzel et al. 1982) that self-quenching of a given level and of a given ion cannot be generalized to other ions in a given crystal. As can be seen, a stronger quenching is found for $LnP_{5}O_{14}$ than for $NaLn(WO_{4})_{2}$ for Tb^{3+} and the opposite is found for Nd^{3+} . The shortest distance between ions is a parameter of less importance than the overlap condition.

In order to understand which is the principal parameter involved in the spatial overlap, let us consider the Nd³⁺ "free-ion" states (fig. 31). Cross-relaxation can take place only if the energy released by ion S(Nd³⁺) is about equal to the energy which can be accepted by ion A(Nd). For two near but "free" ions the energy difference $(e_2 - e_1)$ being negative, such transfer could not take place. For ions in a crystal, the Stark effect can provide the resonance condition: $E_{2M} - E_{1m} = 0$ which, for phonon-assisted transfers, can be extended to $E_{2M} - E_{1m} \ge 0$.

For a "free" Nd³⁺ ion, $(e_2 - e_1)$ is experimentally found to be about a constant (from gravity centers in different materials)

$$(e_2 - e_1) \approx -430 \,\mathrm{cm}^{-1}.$$
 (180)

570



Fig. 31. Free-ion and crystal-field levels of Nd^{3+} involved in self-quenching of ${}^{4}F_{3/2}$ (Auzel 1979).

The resonant condition for cross-relaxation is then:

$$\Delta E_2 - \frac{1}{2}\Delta E_1 + \frac{1}{2}\Delta E_3 = 430 \,\mathrm{cm}^{-1},\tag{181}$$

where ΔE_1 , ΔE_2 , ΔE_3 , are the maximum splitting of ${}^4I_{9/2}$, ${}^4I_{15/2}$, ${}^4I_{3/2}$, respectively.

Stark splittings are usually well described by the potential V at ion sites

$$V = \sum_{k,q,i} B_q^k (C_q^k)_i, \tag{182}$$

where C_q^k are the well-known spherical tensorial operators

$$C_q^k = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_{kq}(\theta, \phi)$$

Considering V as a Hilbert space function, the norm of which N_V (Auzel 1979, 1980b) is given by:

$$N_{V}^{*} = \left[\sum_{k,q} (B_{q}^{k})^{2} \left(\frac{4\pi}{2k+1}\right)\right]^{1/2} \approx N_{V} = \left[\sum_{k,q} (B_{q}^{k})^{2}\right]^{1/2}$$
(183)

with $2J \ge k$, a scalar crystal field parameter can be introduced (Auzel 1979). This scalar parameter is only a quasi invariant (Auzel and Malta 1983) which is however more general and so of wider application than the strict invariants later introduced in crystal-field

theories (Kustov et al. 1980), for which the sum in eq. (183) is taken only over q. Such invariants have been reviewed by Judd (1988).

Good linear relations are experimentally found for maximum splitting, whatever the site symmetry (Auzel 1979), and the resonance condition eq. (181) gives the following solution

$$\Delta E_1 \approx 470 \,\mathrm{cm}^{-1} \quad \mathrm{or} \quad N_V \approx 1800 \,\mathrm{cm}^{-1}.$$
 (184)

 ΔE_1 can easily be deduced from a room-temperature absorption spectrum of the ${}^2P_{1/2}$ state of ${}^4I_{9/2}$, directly giving the Stark splitting of ${}^4I_{9/2}$. Relation (184) simply indicates that weak self-quenching materials will be those with

$$\Delta E_1 < 470 \,\mathrm{cm}^{-1}$$
 or $N_V < 1800 \,\mathrm{cm}^{-1}$.

Examples of such results are illustrated by fig. 32 which at the same time demonstrates experimentally the good linearity between ΔE_1 and N_V . All materials for which both ΔE_1 and B_q^k are available, whatever their site symmetry, are indicated by circled symbols. This figure illustrates a large scale of scalar crystal-field parameters of known materials: the weakest is for NdCl₃, the strongest are for LaOF and YAG.

Although a general theory of melting points of solids (T_m) does not exist up to now, a relation between T_m and N_V has been looked for (Auzel 1979):

$$T_{\rm m} \approx 0.48 N_V + 300$$
 (correlation coefficient 0.88).

Substitution into the criterion of desired N_V shows that weak quenching Nd³⁺-doped materials would be obtained for

$$T_{\rm m} < 1200^{\circ} {\rm C.}$$
 (185)

In another approach, the lattice energy obtained from scratch hardness measurements was tentatively related to quenching: Nd^{3+} -doped materials with small bond strength U/z should show weak quenching (Auzel 1980b)

$$\frac{U}{z} < 500 \,\mathrm{kcal} \,\mathrm{mol}^{-1} \,\mathrm{per} \,\mathrm{bond.} \tag{186}$$

The net result of this investigation is that an increase of the product τN_{θ} can be obtained in weak self-quenching materials. Such materials correspond in the case of Nd³⁺ to those with weak crystal fields which at a guess could be found among low-melting point materials or materials with a high number of constituents preferably with a low scratch hardness. For other ions, self-quenching could be obtained for other conditions of crystal field strength (Auzel et al. 1982); and the N_{V} parameter can still be used to predict the largest Stark splitting, given more generally by (Auzel and Malta 1983)

$$\Delta E = \left[\frac{3g_a}{\pi g(g_a+2)(g_a+1)}\right]^{1/2} \left[\prod_k \left\langle J \left| \left| C^{(k)} \right| \right| J \right\rangle\right]^{1/3} N_V^*,$$
(187)

where g is the J-term degeneracy and g_a is g for J integer and $\frac{1}{2}g$ for J half-integer.



Fig. 32. Maximum ground-state splitting (ΔE_1) of ${}^4I_{9/2}(Nd^{3+})$ versus crystal-field strength (N_V) showing the low-quenching region (Auzel 1979). Data points:

(1) NdP_5O_{14}	(14) LOS (Nd_2O_2S)	(26) KY_3F_{10}
(2) $LiNd(PO_3)_4$	(15) CaF ₂	(27) Nd_2S_2
(3) CLAP	(16) YAlO ₃ (La, Nd)	(28) YVO ₄
(4) $Na_5Nd(WO_4)_4$	(17) $Y_3Al_5O_{12}$ (La, Nd)	(29) PbMoO ₄
(5) Na(La, Nd)(WO ₄) ₂	(18) $Ba_2MgGe_2O_7$	(30) LiNbO ₃
(6) $K_3Nd(WO_4)_4$	(19) NdNb ₅ O ₁₄	(31) phosphate glass KLi
(7) Na ₅ Nd(MoO ₄) ₄	(20) silicate flint glass	(32) KY(MoO ₄) ₂
(8) (NAB)NdAl ₃ (BO ₄) ₃	(21) $Gd_{17}NdO_3(MoO_4)_3$	(33) $CaAl_4O_7$
(9) $Na_{18}Nd(BO_3)_7$	(22) $Li(Y, Nd)F_4$	(34) La_2O_3
(10) NdCl ₃	(23) (Nd, La)F ₃	(35) LaOF(Nd ³⁺)
(11) (Bd, La)Ta ₇ O ₁₉	(24) $Nd(C_2H_5ZO_4)_3$ 9H ₂ O,	(36) WO ₄ Ca
(12) LiNdNbO ₄	weak field quenched by H_2O	(37) Cl ₃ Nd in ice.
(13) tellurite glass	(25) $Ca_5(PO_4)_3F$ (FAP)	

Reduced matrix elements for the Nd^{3+} laser transition at 1.06 μm				
λ	$\left< {}^{4}\mathrm{I}_{11/2} \left \left U^{(\lambda)} \right \right {}^{4}\mathrm{F}_{3/2} \right>$			
2	0			
4	0.3769			
6	0.6408			

Table 5

4.1.3. Optimization of line strength and cross-section

The next step in trying to increase M is to increase cross-sections for absorption and emission while keeping τ high enough. From what we have seen in sect. 3.1.1, we know that for trivalent lanthanides, oscillator strengths are caused by odd crystal-field parts contained in the parameters. However, except for centrosymmetric sites as obtained in Cs₂NaLnCl₆ crystal types (Tofield and Weber 1974), the oscillator strength can be expected to vary a great deal only for hypersensitive transitions (with $\Delta J \leq 2$); this is not the case for laser transitions from ${}^{4}F_{3/2}$ in Nd³⁺. For emission at ~1.06 μ m, the matrix elements involved are given in table 5.

From T_{λ} , determined by oscillator strength measurements in absorption, it is possible to obtain the laser transition oscillator strength from table 5 and eq. (123). It has been verified that the result is nearly constant for non-centrosymmetric crystals (Auzel and Michel 1975), as shown in table 6 where the integrated cross-section has been obtained using eqs. (117) and (121). Using the average value of 3.7×10^{-18} cm, an estimate of the laser cross-section for any Nd³⁺-doped material can be obtained as (Auzel 1987)

$$\sigma_0 = \frac{g_1}{g_2} \times 3.74 \times 10^{-18} \times \Delta \bar{\nu}^{-1},$$

where $\Delta \bar{v}$ is the effective homogeneous linewidth as given by eq. (172). Since

$$\frac{g_1}{g_2} \approx \frac{2J_1 + 1}{2J_2 + 1} = 3$$
 for 1.06 µm

it follows that

$$\sigma_{0(\rm cm^2)} = 11.2 \times 10^{-18} \left(\Delta \bar{\nu}_{\rm (cm^{-1})} \right)^{-1}.$$
(188)

The effective homogeneous linewidth means that though the line structure be inhomogeneous due to the existence of various crystal sites, it can still be considered homogeneous when laser takes place for times longer than required for energy transfer between sites. Application of eq. (188) is presented in table 7 for different types of laser materials. This table shows the validity of eq. (188) within a factor two for materials as different as glasses and crystals.

COHERENT EMISSION IN RARE-EARTH MATERIALS

Hostf (in 10-6) ${}^{4}I_{11/2} \rightarrow {}^{4}F_{3/2}$ $\int \sigma(\mathbf{v}) d\mathbf{v}$ (in 10-18 cm) $Ca_{10}(PO_4)F_2$ (FAP)3.034.2 $Nd_2P_5O_{14}$ (NdUP)2.633.5 $Y_3Al_5O_{12}$ (YAG)2.593.5

Table 6 Oscillator strength and integrated cross-section for the $1.06\,\mu m$ laser transition in various hosts

			Table 7			
Estimation of σ_0	through eq.	(187) and	comparison	with measurements	for Nd ³⁺	at ~1.06 µm

Material	$\Delta \overline{\mathbf{v}} (\mathrm{cm}^{-1})$	$\sigma_0 (10^{-20} \mathrm{cm}^2)$			
		Eq. (187)	Measurement	Reference	
Phosphate glass (P_2O_5 , Na_2O , K_2O , CdO)	214	5.2	4.4	Michel et al. (1978)	
Tellurite glass (TeO ₂ , Li ₂ O)	240	4.6	4.7	Michel et al. (1978)	
Fluorozirconate glass (ZrF_4 , BaF_2 , LaF_3)	264	4.2	3	Stokowski et al. (1978)	
Fluorophosphate glass LG 810	310	3.6	2.6	Stokowski et al. (1978)	
Silicate glass LG 650	343	3.2	1.1	Stokowski et al. (1978)	
(NdUP) $Nd_2P_5O_{14}$	127	8.8	8.2	Singh et al. (1975a)	
(LNA) LaMgAl ₁₁ O ₁₉	105	10.7	10	Singh et al. (1975a)	
(YAG) Y ₃ Al ₅ O ₁₂	68	16.5	33	Kaminskii (1981)	

A more precise, yet simple, determination of σ_0 can be obtained by taking into account slight variations in ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ oscillator strengths (Deutschbein 1976). From Judd's theory (eq. 123), the 1.06 µm transition strength can be written as

$$S_{1.06\mu m} = \Omega_6 (0.407 + 0.142X), \tag{189}$$

where the relationship (125) for Ω_{λ} has been used and X is the ratio Ω_4/Ω_6 , sometimes called "spectroscopic quality parameter" (Kaminskii 1981). S is defined by

$$S(J \to J') = \frac{3h(2J+1)}{8\pi^2 m} \frac{f}{v} = \sum_{\lambda} \Omega_{\lambda} \left| \left\langle J' \left| \left| U^{(\lambda)} \right| \right| J \right\rangle \right|^2.$$
(190)

Considering the strength of the absorption transitions ${}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}$, ${}^{4}S_{3/2}$ at 0.750 µm,

$$S_{0.750\mu\rm{m}} = \Omega_6 (0.6597 + 0.045X), \tag{191}$$

eliminating Ω_6 between eqs. (189) and (191), and assuming $X \leq 1$, one obtains:

$$\sigma_0 = \frac{2.7S_{0.750}}{\Delta \tilde{\lambda}} \quad (\text{in } 10^{-6} \,\text{cm}^2). \tag{192}$$

This relationship gives the laser cross section from a single integrated absorption measurement at about $0.750 \,\mu\text{m}$ and from the emission effective linewidth at $1.06 \,\mu\text{m}$, with good accuracy (Deutschbein 1976).

F. AUZEL

The width $\Delta \bar{v}$ is caused by the existence of various crystal sites for active ion as well as by crystal strains and their modulation by crystal vibrations. Statistical broadening is usually large where charge compensation is necessary. Also such perturbative effects will be stronger for materials with a large crystal field, that is for large N_V . Weak electron-phonon coupling is favorable as well as high sound velocity or high Debye temperature (Kushida 1969), which means high phonon cut-off frequencies. This last point is incompatible with a high efficiency from a non-radiative point of view and then a compromise has to be found.

Because of eq. (127), the lifetime is inversely proportional to all oscillator strengths connecting the emitting level ${}^{4}F_{3/2}$ to ${}^{4}I_{11/2}$, ${}^{4}I_{13/2}$, ${}^{4}I_{15/2}$, ${}^{4}I_{9/2}$,

$$\frac{1}{\tau_0} = A_{11/2} + A_{13/2} + A_{15/2} + A_{9/2},$$

and the highest τ will be obtained for $\tau = \tau_0$, that is for negligible non-radiative transitions; also for given $A_{11/2}$, the largest τ_0 is obtained for small $A_{13/2}$ and $A_{15/2}$, which means a high branching ratio for ${}^{4}I_{11/2}$. Substituting eq. (123) into eq. (126), the branching ratio can be written as (Kaminskii 1981)

$$\beta_{JJ'}(X) = \frac{(a_{J'}X + b_{J'})/\bar{\lambda}_{J'}^3}{\sum_{J'} (a_{J'}X + b_{J'})/\bar{\lambda}_{J'}^3},$$
(193)

where

$$a_{J'} = \left| \left\langle {}^{4}\mathbf{F}_{3/2} \left| \left| U^{(4)} \right| \right|^{4} \mathbf{I}_{J'} \right\rangle \right|^{2}, \quad b_{J'} = \left| \left\langle {}^{4}\mathbf{F}_{3/2} \left| \left| U^{(6)} \right| \right|^{4} \mathbf{I}_{J'} \right\rangle \right|^{2}, \quad J' = \frac{15}{2}, \frac{13}{2}, \frac{11}{2}, \frac{9}{2}.$$

A plot of $\beta_{JJ'}$ versus the spectrometric quality parameter X is shown in fig. 33. It shows that the maximum value for $\beta_{3/2,J'}$ for the 1.06 µm emission is 0.66, and that for the 1.32 µm emission is 0.17 for X = 0. On the contrary, $\beta_{3/2,9/2}$ for the emission at 0.9 µm can reach 0.75 for high values of X. Then for the usual laser emissions at 1.06 µm as well as 1.32 µm, X should be as small as possible.

X can be simply obtained by

$$X = 1.23 \frac{S({}^{2}P_{1/2})}{S({}^{4}I_{15/2})},$$
(194)

through measurement of the ratio of two absorption intensities (Kaminskii 1981). The experimental value of X ranges from 0.22 for CaF_2-CdF_3 mixed crystals to 1.5 for YScO₃ (Kaminskii 1981), with X = 0.3 for YAG (Y₃Al₅O₁₂) and YALO (YAlO₃), or "YAP" (yttrium-aluminium-perovskite) as it is now called.

Having looked for the smallest X, τ/τ_0 has to be increased as nearly as possible to unity. From eq. (129) and a given ΔE , $\hbar\omega_m$ has to be minimized for two reasons: (i) in order to increase the multiphonon order ($N = \Delta E/\hbar\omega_m$), and (ii) because $\bar{N}S_0 \approx cte \approx 82:\alpha_s$ is the highest for materials with smallest $\hbar\omega_m$ (Auzel 1978).

576



Fig. 33. Branching ratios for ${}^{4}F_{3/2}$ emission in Nd³⁺ versus spectroscopic quality parameter X (from Kaminskii 1978).

Then, non-radiative transition for Ln^{3+} will be minimized for soft materials with heavy constituents and materials without high vibration energy complexes involving such light atoms as hydrogen: OH⁻ is a very detrimental species for a laser material. For instance, fluorophosphate glasses were found to be efficient laser glasses for IR emission (Auzel 1969a), as they dissolve only small quantities of OH⁻. For the same reason materials obtained by the sol–gel method (Brandel et al. 1991) may be of limited interest because one can foresee that quantum efficiencies shall be very small, except for $Eu^{3+}(^{5}D_{0})$ and $Tb^{3+}(^{5}D_{4})$, because the glass will retain too much of the initial solvent.

4.2. The high-power laser case

4.2.1. Thermal properties for high average power lasers

When high CW power or high average power in pulsed lasers is required, thermal properties have to be considered. Besides the considerations of the previous section, two quantities are of importance: thermal conductivity and thermal variation of optical path; the first allows for good cooling of the laser material, the second avoids the thermolensing process which perturbs the optical cavity setting.

Both expansion (α) and conductivity (K) are linked to a cubic anharmonic term in the potential of a lattice vibration (Klemens 1958). An estimation can be obtained by the Leibfried-Schloemann formula (Leibfried and Schloemann 1954)

$$K \approx \frac{6}{10} \frac{(4)^{1/3}}{\gamma^2} \left(\frac{3k}{h}\right)^3 M a \frac{\Theta^3}{T},\tag{195}$$

where a^3 and M are, respectively, the volume and mass per atom, γ is the cubic coefficient for non-harmonicity, Θ is a Debye temperature such as $\hbar\omega_m \approx \Theta_k$, and T > 0. Then good thermal conductivity is linked with high maximum phonon frequency; this has to be compromised with good quantum efficiency. Hopefully the transition at 1.06 µm in Nd³⁺ corresponds to a large ΔE with respect to $\hbar\omega_m$. For other transitions at longer wavelength in other ions, this may be more difficult to deal with. In glassy matrices, though there exist high-energy vibrations corresponding to glass-forming oxygen links, thermal conductivity is limited by crystallite size.

K has been given more generally by (Kittel 1971)

$$K = \frac{1}{2}C\nu\ell,\tag{196}$$

where C is the specific heat (~3 Nk above room temperature), v is the average phonon velocity, and ℓ is the phonon mean free path. For glasses, ℓ is limited by the crystallite size which reduces K by an order of magnitude with respect to crystals: $KT = 45 \text{ W cm}^{-1}$ for quartz versus $KT \approx 3.8 \text{ W cm}^{-1}$ for fused quartz (Kittel 1971), though Si–O vibration frequency still mediates the non-radiative transitions for both. This is a definite drawback for glasses as high average power laser materials.

The thermal expansion (α) which plays a role in optical path stability is linked to the same anharmonic cubic coefficient γ as conductivity (Klemens 1958)

$$\alpha = \frac{\partial x}{\partial T} \approx \frac{\gamma}{\lambda} \sum_{k} C(k),$$

where λ is the compressibility, and C(k) is the specific heat for phonon mode k. Large anharmonicity γ increases thermal expansion and reduces thermal conduction. However most materials with small anharmonicities have to be looked for. However, since most substances have similar γ -values, the thermal conductivity is sensitive to Θ . The smallest thermal expansions have been obtained in composite materials such as glass ceramics which may also be used as active ions hosts (Müller and Neuroth 1973). Such glass ceramics would be very interesting as laser materials in case active ions stay inside crystallites smaller than the wavelength rather than in both glassy and crystalline phases (Auzel et al. 1975, Santa-Cruz et al. 1994, 1995). Because the laser properties of crystals can be obtained microscopically, although in a macroscopic glass form, it has an inherent technological advantage for the production of large lasers. However, thermal conductivity at high average power would still be a problem.

As for the variation of the refractive index with temperature, from the Sellmeier formula one knows that $n^2 - 1 = kd$, where d is the material density and k is a proportionality coefficient. One then obtains

$$\frac{\partial n}{\partial T} = -\frac{3}{2}kMa^{-4}\alpha = -\frac{3}{2}kd\alpha,\tag{197}$$

showing that the optical path shall be thermally more stable for a lower dilatation material with lower density and lower index of refraction. All thermal properties could be usefully obtained from photothermal experiments (Boccara 1987).

4.2.2. Optical properties for high peak power and high power density lasers

When high peak power is looked for, this is usually obtained at the expense of pulse length by Q-switching or mode-locking processes. This in turn requires a long time τ in order to store energy between laser pulses, and large $\Delta \bar{\nu}$ in order to couple a great number of cavity modes. This is caused by a modification of the spectral requirements found for CW lasers. On the other hand, a low gain is sometimes looked for in order to avoid a laser effect when the cavity Q is spoiled, otherwise not enough energy could be stored. Moreover, nonlinear optical effects are encountered at high peak power, introducing a novel kind of loss: part of the energy at laser wavelength is up-converted by harmonic generation and/or by energy transfers between excited states (APTE effect).

The refractive index of a material subjected to an intense electric field is

$$n=n_0+n_2E^2,$$

where E is the amplitude of the optical electric field linked to the optical intensity by

$$I=\frac{n_2E^2}{\gamma},$$

where for an isotropic medium such as a glass (Stokowski et al. 1978)

$$\gamma = \frac{K(n_{\rm D} - 1)(n_{\rm D}^2 + 2)^2}{n_{\rm D}\nu \left[1.52 + (n_{\rm D}^2 + 2)(n_{\rm D} + 1)\nu/6n_{\rm D}\right]^{1/2}},$$
(198)

where $K = 2.8 \times 10^{-18} \text{ m}^2/\text{W}$, n_D is the index of refraction for the sodium line at 589.3 nm, and v is the Abbe number. The nonlinear index is obtained from γ by

$$n_2 (\mathrm{esu}) = \frac{c_0 n}{40 \pi} \gamma \,(\mathrm{m}^2/\mathrm{W}).$$

 γ and n_2 are increasing functions of n_D and decreasing functions of $v = (n_D - 1)/n_F - n_C$; n_F and n_C are the refractive indices at 486.1 and 656.3 nm. Typical values are:

BeF ₂	$n_{\rm D} = 1.27$	v = 107	$\gamma = 0.7 10^{-20} \text{m}^2/\text{W}$
SiO ₂	$n_{\rm D} = 1.46$	v = 67	$\gamma = 2.6 \ 10^{-20} \ m^2/W$

It is seen that for high peak power applications a low refractive index is required. In the crystal case, to avoid SHG (second-harmonic generation), a centro-symmetric structure has to be searched for, because the so-called Miller rule (Miller 1964) gives for the allowed elements of a nonlinear susceptibility tensor for second-harmonic generation.

$$d_{ijk}^{2\omega} = 1.1 \times 10^{-9} (4\pi)^3 \chi_{ii}^{2\omega} \chi_{ij}^{\omega} \chi_{kk}^{\omega} \text{ (esu)},$$
(199)

where χ are linear susceptibilities for beam frequency directions i, j, k in the crystal, directly connected by $(n^2 - 1) = \chi$ with linear refractive index at 2ω and ω .

Such coherent nonlinear effects may also induce gain losses by the self-focusing effect, destroying the desired mode properties of the optical cavity. A power threshold has been estimated by Yariv (1967)

$$p_{\rm c} = \frac{\varepsilon_0 n^3 c_0 \lambda^2}{4\pi n_2} \quad ({\rm mks}), \tag{200}$$

with ε_0 the vacuum permittivity.

In some cases, the nonlinear effect of the R-doped host is looked for in order to obtain "self-doubling visible lasers": the output of the laser is at twice the frequency of the R-laser transitions, the matrix being purposely non-centrosymmetric in order to have a large n_2 . For such a laser, the cavity mirrors are both R_{max} at the fundamental frequency, and one of them is partially transparent at its harmonic in order to insure the output coupling. This type of laser has been reviewed by Kaminskii (1981) except for the recent optical confinement (Li et al. 1988) point of view.

5. Recent advances in R lasers

5.1. R-doped fibers for amplifiers and lasers

The first laser sources based on optical fibers were demonstrated by Snitzer as early as 1961 (Snitzer 1961). In 1974, Stone and Burrus (1974) obtained the first diode-pumped laser fiber. However, it is only since 1990 that the field is, we could say, "exploding". This interest takes its roots in the recent success obtained in producing useful amplifiers at $1.5 \,\mu$ m, a wavelength of recognized interest for long- and medium-distance optical communications. Within three years, Er^{3+} -doped silica fibers, "born" in laboratories, became commercially available. Even a bibliography dealing only with EDFA (Erbium Doped Fiber Amplifiers) has appeared (Sunak 1991).

The basic advantage of R-ion doped fiber as an amplifier medium is due both to the small core size and to the low R-ion concentration required; linked with the optical confinement maintained over a great length, this leads easily to absorption saturation even at a low level of pumping (a few 100 mW). This allows 3-level amplification under continuous excitation at room temperature (Mears et al. 1986). Because several books have recently been published on this now extensive and important subject (Digonnet 1993, Desurvire 1994, Becker et al. 1996), we shall present here only a few basic features and remarks.

5.1.1. The peculiar case of fibers for 3-level amplifiers and lasers

In sect. 2.2.3 we briefly recalled the threshold flux condition for 4-level systems (eq. 118). In the 3-level case, when the final state for laser emission is the ground state or has noticeable population, the threshold condition becomes

$$\varphi_{\rm th} = \frac{1}{2\tau} \frac{h v_{\rm p}}{\sigma_{\rm p}},\tag{201}$$

and the Figure of Merit (Auzel 1987) is now written as

$$M_3 = \tau \sigma_{\rm p},\tag{202}$$

where $\tau = \eta T_1$ is the measured transition lifetime.

So, a good 3-level material requires a large lifetime τ together with a large absorption cross-section (σ_p) at pumping wavelength. A good 4-level material requires a large product at the emission transition together with a large concentration and large absorption cross-section. However τ , $\tau \sigma_0$, and N_0 , being correlated, have to be optimized by their product.

Because of the weak concentration of active ions usually doping fibers, one may ask to what extent the classical approximation (see sect. 2.2.3)

$$\frac{N_0}{2} + \Delta N \approx \frac{N_0}{2},\tag{203}$$

holds (Auzel 1993). For the usual concentration range in fiber, ranging typically from 100 to 1000 ppm (about $10^{17}-10^{18}$ cm⁻³), σN_0 is of the order of $10^{-2}-10^{-4}$ cm⁻¹ for the typical cross-sections of $10^{-20}-10^{-21}$ cm² found in R-ion doped glasses. Then for fibers with intrinsic losses of e.g. 1 dB/km, an absorption coefficient of 10^{-5} cm⁻¹ is largely negligible in comparison with reabsorption losses $\sigma N_0/2$. However, such losses may reach 10^{-3} cm⁻¹ for intrinsic glass losses of 434 dB/km. In such a case, the approximation of eq. (203) does not hold anymore.

On the other hand, in a laser the essential loss is the necessary and useful coupling to the outside. This loss can be considered as distributed over the medium length L. One has for the loss α of an output mirror of reflectivity **R**

$$\alpha = \frac{\log R}{L},\tag{204}$$

which gives e.g. 10^{-3} cm⁻¹ for L = 1m, and output coupling of 10% (R = 90%).

So, for shorter fibers and "natural" coupling (Fresnel reflection), α may be still larger and eq. (203) does not hold. Then the flux at threshold, even for a 3-level scheme, introduces the 4-level term of the bulk case

$$\Phi_{t} = \frac{h\nu_{p}}{\sigma_{p}\nu} \left[\frac{1}{2\tau_{0}} + p\frac{g_{1}}{g_{2}} \frac{1}{N_{0}} \right].$$
(205)

Nothing basic is changed by the fiber shape in comparison to the bulk case except the fact that the necessary Φ_t is more easily reached (small fiber cross-section S) and maintained over large L. The impact of this optical confinement has an essential role in fiber amplifiers and lasers, so much so that the fiber is single-mode.

5.1.1.1. Fiber intrinsic properties.

5.1.1.1.1. The single-mode condition (Cozannet et al. 1981). Defining a quantity V by

$$V = \frac{2\pi a}{\lambda} (n_1^2 - n_2^2)^{1/2},$$
(206)

the single-mode condition is

$$V \leqslant 2.405,\tag{207}$$

where a is the fiber core radius with a refraction index n_1 ; n_2 is the refractive index of the cladding. Equivalently, this single-mode condition for the core diameter is written

$$2a < \frac{2.4\lambda}{\pi(\mathrm{NA})},\tag{208}$$

where $(NA) = (n_1^2 - n_2^2)^{1/2} \sin \Theta_c$ is called the "Numerical Aperture" of the fiber, and Θ_c is the input critical half-angle. As an example, a single-mode fiber in the visible would have the following specifications: $\lambda_c = 0.55 \,\mu\text{m}$, $(n_1 - n_2) = 8 \times 10^{-3}$, giving $2a = 2.5 \,\mu\text{m}$. With such a small diameter, one understands why pumping threshold fluxes may be easily reached even at moderate pumping power of a few hundred mW.



Fig. 34. Theoretical absorption windows of undoped silica and fluoride fibers.

5.1.1.1.2. Transmission properties. The recent interest in erbium- (Er^{3+}) doped fiber amplifiers (EDFA) originates from the recognized fact that the optical fiber transmission windows for silica or fluoride glasses (fig. 34) are in tune with the wavelengths of the two Er^{3+} transitions: ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ at 1.5 µm, and ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ at 2.7 µm.

5.1.1.2. Spectroscopic properties of fibers: comparison with bulk samples.

5.1.1.2.1. Absorption. Because high pumping fluxes are easily reached at levels of about 0.2 MW cm⁻², absorption saturation at a doping level of even 1000 ppm is readily obtained; it deforms the absorption spectra in comparison with bulk results; so studying a fiber, it is difficult to measure the real spectroscopic absorption coefficient and line shape of a R transition as illustrated by fig. 35 even at 50 mW input level (Auzel 1993).



Fig. 35. Comparison of bulk and fiber glass absorption spectra of Er^{3+} at different input power levels (Auzel 1993).

5.1.1.2.2. *Emission*. When the fiber and pumping are long and large enough to obtain gain, emission spectra are deformed by amplification by stimulated emission (ASE) (fig. 36). So, observed longitudinal emission spectra may be very different from bulk



Fig. 36. Emission spectrum at $2.7 \,\mu\text{m}$ of a bulk sample as compared with the ASE-modified emission spectrum of a fiber (Auzel 1993).

F. AUZEL

spectra and are parametrically dependent both on excitation level and fiber length. As such, the spectrum obtained may be different from the gain spectrum when the signal is larger than the spontaneous emission noise.

5.1.1.2.3. Radiative energy transfer. When resonance transitions are considered, which exist both in emission and in absorption as is the case in a 3-level scheme, emitted photons may be successively reabsorbed and so recycled several times. This is a radiative energy transfer which is known to depend critically on the geometrical conditions of the experiment (Auzel 1969a). In a doped fiber, the optical confinement dramatically increases this effect for longitudinal lifetime measurements (τ) of the ${}^{4}I_{13/2}$ manifold of Er³⁺. Such τ measurements are often used to obtain η , consequently care has to be taken not to obtain too large quantum efficiencies. This implies a lifetime measurement on a bulk sample or transversely to the fiber, and at short distance from excitation. These last measurements are often difficult because of the weakness of the emission signal.

5.1.1.3. Adequacy of fibers for laser diode pumping. Considering typical values for the NA of a single-mode fiber, (NA)=0.15 rad for $(n_1 - n_2) = 8 \times 10^{-3}$, this gives 17° for the acceptance angle. Such values are not far from emission angles of pumping laser diodes. For example, pumping diodes at 1.48 µm have typical emission angles of about 15° (parallel to the junction plane) and 20° (perpendicular to the junction plane). On the other hand, the monochromaticity of the diode can be adapted to R absorption bands, which drastically increases the overall efficiency in comparison to black body or arc-lamp pumping sources. Values currently available for commercial YAG lasers are significant. The overall efficiency can be 6% for a diode-pumped YAG versus 0.04% for a quartziodine-lamp-pumped YAG. This adequacy of a laser diode for the pumping of a R-doped material is one of the recent advances in the field as demonstrated by table 8.

Comparison of various pumping sources for the Nd ³⁺ :YAG laser							
Pumping source	Electric power (W)	Optical pumping power (W)	Single-mode laser power (W)	Total efficiency (%)	Pump lifetime (h)		
Rare gas arc lamp	2000	100	8	0.4	400		
Iodine tungsten lamp	500	5	0.2	0.04	100		
Laser diode	1	0.2	0.06ª	6	5000		

Table 0

^a Projects exist for CW laser output of 500 W.

5.1.2. Basic comparison between silica and fluoride fibers

When changing the glass matrix, the radiative probabilities of R ions are less modified than the non-radiative ones. Consequently, the latter have to be considered first when optimizing a given ion-glass system. Although theories on non-radiative transitions are



Fig. 37. Lower energy levels of Er^{3+} and theoretical transition probabilities for a silica and a fluoride glass (Auzel 1990).

rather complex, for R ions a useful simplification of the nonadiabatic Hamiltonian theory gives the following expression, refined with respect to the simplified approach of eq. (129) of sect. 3.2 (Auzel 1991)

$$W_{\rm NR} \approx 6.6 \times 10^7 (n+1)^{\Delta E/\hbar\omega_{\rm m}} \exp - \alpha (\Delta E - 2.4\hbar\omega_{\rm m}), \tag{209}$$

giving the order of magnitude (in s⁻¹) for $W_{\rm NR}$. The "effective" energy of vibration, $\hbar\omega_{\rm m}$, generally corresponds to the highest vibration frequency of the host; α is a parameter ranging from 3 to 6×10^{-3} cm. Practically, $\hbar\omega_{\rm m} = 580$ cm⁻¹ for a fluorozirconate glass (ZBLAN), that is a ZrF₄-BaF₂-LaF₃-AlF₃-NaF glass, and about 1100 cm⁻¹ for a silica glass. ΔE is the energy difference with the electronic state just below the one under consideration.

Figure 37 gives typical values for the transitions of Er^{3+} of interest for optical communications. These calculated values predict that at 1.5 µm, fluoride fibers have a larger quantum efficiency than those made of silica, though 100% is often assumed for silica. Also they show that if 0.98 µm radiation can be a useful pumping wavelength in silica, 1.48 µm alone has to be used for fluoride glasses. At 2.7 µm, only fluoride glasses may be used as amplifiers or lasers.

In general, fluoride glasses give more metastable levels for a given ion, so more levels could be used as relays in up-conversion either by excited absorption (ESA) or by energy transfers (APTE effect) (see sect. 3.4). As we have seen, this last process is linked with the condition $W_{SA} \ge 1/\tau_c$, where W_{SA} is the transfer probability from ion S to ion A.

Such effects, which can take place in multiple sequences, will be favored in fluoride glasses. Further, they are nonlinear effects and obey an nth-power law for a process of order n, and thus are even more sensitive to the optical confinement of the fiber.

It is observed that for the 2.7 μ m transition in Er³⁺, the quantum efficiency of a fluoride glass can be much larger than in a YAG:Er³⁺ crystal which is known however to be a commercial laser material. So a CW laser effect at 2.7 μ m was obtained even in the bulk



Fig. 38. Laser emission spectrum near $2.7 \,\mu$ m for a bulk glass at various pumping levels (Auzel et al. 1988b).

(Auzel et al. 1988b) with the possibility to have some wavelength tuning (fig. 38) over the inhomogeneous lineshape of the Er^{3+} transition in the glass structure. Such a possibility is used in glass-fiber lasers, which can show some tunability as we shall see in sect. 5.1.3.

5.1.3. Examples of doped fiber amplifiers and lasers

Although the historical experiment of 1961 introduced Nd^{3+} for doping fibers (Snitzer 1961), it is essentially the use of Er^{3+} which recently gave the impulse to fiber amplifiers and lasers.



Fig. 39. Schematic of the first CW room-temperature 3-level laser (Mears et al. 1986).



Fig. 40. Schematic of the first diode-pumped 1.5 µm fiber amplifier (Reekie et al. 1987).

5.1.3.1. Er^{3+} in silica glass at 1.55 µm. The landmark experiment was that by Mears et al. (1986) who obtained a tunable laser at 1.53 µm in a silica fiber. It was the first CW 3-level laser operating at room temperature, which is why this experiment is so important. Figure 39 gives the general scheme for this laser. For a pumping power of 90 mW at 0.514 µm (argon laser), 0.3 mW was obtained at 1.53 µm. This experiment opened the door to many 3-level lasers and amplifiers. Transitions even unknown as lasers in crystals could show a laser effect in a glass fiber; this was the case for Er^{3+} at 1 µm (${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$) (Allain et al. 1989).

In 1987, another important step was the laser diode pumping; Reekie et al. (1987) expected to pave the way for inline amplification at $1.5 \,\mu$ m, which was later demonstrated to be true. That same year they obtained the first fiber amplifier at $1.5 \,\mu$ m (Mears et al. 1987) (fig. 40), giving a gain of 28 dB for a length of 3 m, with an amplification bandwidth of more than 4 THz (30 nm).

Soon after these first experiments many others followed (Desurvire et al. 1987, 1989, Olskansky 1988, Giles et al. 1989), showing that a gain of 30 dB could be obtained with a noise factor of only 0.2 dB above the quantum limit of 3 dB. As early as 1989, transmission experiments at the rate of 1.2 Gbit over 267 km were described (Edagawa et al. 1989), together with a first experiment undersea showing the advantages of Er^{3+} -doped silica fiber amplifiers over semiconductor ones (Wakabayashi et al. 1989): a gain of 20 dB per amplifier versus 7.5 dB, respectively, and a larger saturation power for the fiber amplifiers. The erbium-doped silica fiber amplifier (EDFA) was then rapidly considered as the technology for long distance transmission and was selected as early as 1990 as

the technology for new undersea cables. EDFA could also be used to upgrade existing links by short-circuiting existing repeaters at 1.3 μ m by EDFA at 1.5 μ m (Boggis et al. 1991). This whole new field has been reviewed by Digonnet (1993), Desurvire (1994), and Becker et al. (1996).

5.1.3.2. Heavy fluoride glasses doped with Er^{3+} , Pr^{3+} , Tm^{3+} . Owing to the high quantum efficiencies observed in heavy metal fluoride glasses in the near IR and particularly at 2.7 μ m (Auzel et al. 1988b), the laser effect has been obtained at this wavelength in an Er^{3+} -doped ZBLAN fiber (ZrF₄, BaF₂, LaF₃, AlF₃, NaF) under argon-ion laser pumping at 476 nm (Brierley and France 1988). Gain reaches 35 dB at 2.7 μ m in a ZBLAN: Er^{3+} fiber of 3 m length when pumped by a dye laser at 620 nm (Ronarc'h et al. 1991a). The gain specifications in such an amplifier are given in fig. 41.

However, a ZBLAN: Er^{3+} glass fiber also appears particularly interesting for 1.5 µm amplification. Linked with the high quantum efficiency (100%) of Er^{3+} at 1.5 µm in a ZBLAN glass, a gain of 30 dB has been recently obtained. Figures 42 and 43 give the general specifications of this amplifier (Ronarc'h et al. 1991b).

The most important feature of Er^{3+} -doped heavy fluoride glass fiber amplifiers is the flatness of their gain behavior, which permits the very wide band amplification (over about 25 nm) required for wavelength division multiplexing (WDM) encompassed for future long-haul optical communication networks (Marcerou et al. 1992, Ronarc'h et al. 1991b, Clescla et al. 1994a). Because of this gain flatness, linked with the weaker crystal field at Er^{3+} sites with respect to silica glass (Auzel et al. 1993), the overall bandwidth can be maintained over a cascading of many amplifiers (Clescla et al. 1994b).

Figure 44 presents the gain profile over four fluoride glass amplifiers (a) compared to four silica glass amplifiers (b), obtained after sixteen optical equalized carriers, between 1533.7 and 1558.2 nm, were injected at the entrance of a transmission system



Fig. 41. Gain curve of an optimized fluoride fiber amplifier near $2.7 \,\mu m$ (Ronarc'h et al. 1991a).



spanning 440 km with an amplifier separation of about 100 km. Each channel allowing an information rate of 2.5 Gbits s⁻¹, such a system has a record potential bit-rate–distance product of 17.6 Tbits s⁻¹ km⁻¹ (Gain Project, 1994).



Fig. 44. Evolution of spectrum at output of (a) 4th cascaded fluoride amplifier, and (b) 4th silica amplifier (Gain Project 1994).

Recently, following the interesting results obtained at $1.5 \,\mu\text{m}$ with Er^{3+} in fibers, needs for short-distance distribution at $1.3 \,\mu\text{m}$ were considered. In fact, amplifiers are necessary to boost the signal power after a multiway branching junction. Activity in this field is increasing rapidly and a gain of 38 dB was obtained in small-core ZBLAN glass fibers doped with Pr^{3+} . A pumping power of 300 mW at $1.02 \,\mu\text{m}$ was obtained from a Al_2O_3 :Ti³⁺ laser (Miyajima et al. 1991). Since then, boxed Pr^{3+} -doped fluoride fiber amplifier (PDFFA) prototypes with solid-state diode pumping have been produced, providing 30 dB gain, high output power (250 mW), and low noise (4 dB) (Gain Project 1994).

In the Pr^{3+} case, only fluoride glasses or lower phonon glasses can be considered because the ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$ transition has a very low quantum efficiency in a high-phononenergy material, such as silica glass (see sect. 5.1.2).

In local area transmission networks ("fiber to the home"), there is a need for lowprice amplifiers to overcome splitting losses. Because low-price transmitters and receivers already exist at 0.8 µm as already produced for the compact disc entertainment market, there is a need for 0.8 µm amplifiers. Such amplifiers can be obtained from ZBLAN:Tm³⁺ fibers (Carter et al. 1991, Lauder et al. 1993). In such a system the ${}^{3}F_{4} \leftrightarrow {}^{3}H_{6}$ transition is involved both for pumping at 790 nm and amplification between 810–830 nm, realizing a quasi 4-level system (Carter et al. 1991). Above a 100 ppm doping level, self-quenching takes place by a (${}^{3}F_{4}-{}^{3}H_{6}$) \rightarrow (${}^{3}H_{4}-{}^{3}H_{4}$) cross-relaxation (see sect. 3.3.1). A Tm³⁺ amplifier at 0.8 µm is particularly promising with a high gain efficiency (2.4 dB gain for 1 mW pumping at 780 nm) providing a gain of 26 dB with output power of +13 dBm at launched pumping power of 31 mW; this corresponds to an overall gain of 65% (Percival et al. 1994).

5.2. Up-conversion lasers

Usual lasers respect Stokes' law, the pump excitation being at a higher energy than emission. Because present-day high-power semiconductor laser pumping sources are limited to the red or infra-red region, one anticipates that it is impossible to obtain directly an all-solid-state laser system in the visible. To circumvent this limitation one can make use of second-harmonic generation, APTE (see sect. 3.4.2), or ESA when optical confinement increases its probability. These processes are basically of an anti-Stokes nature.



Fig. 45. Energy scheme of the upconversion diode pumped laser (after Tong et al. 1989).

5.2.1. Anti-Stokes lasers in crystals

This type of pumping would provide solid-state laser operation in the visible using the now well-developed IR semiconductor pumping source, and such anti-Stokes lasers could be used for high-density compact disc memories. The first results in APTE anti-Stokes lasers were obtained a long time ago for the Yb^{3+} - Er^{3+} and Yb^{3+} - Ho^{3+} systems in BaY_2F_8 crystals (Guggenheim and Johnson 1971). Anti-Stokes lasers were then obtained under pulsed flash pumping. More recently, CW up-conversion lasers emitting in the green part of the spectrum have been obtained under IR laser diode pumping (Tong et al. 1989) of LiYF₄: Er^{3+} , causing a renewed interest in APTE up-conversion (fig. 45).

However, such up-conversion lasers in crystals are still limited to low temperatures for CW operation (Tong et al. 1989, Hebert et al. 1990, Macfarlane et al. 1988, Scott et al. 1993, Stephens and Macfarlane 1993), because the laser schemes are generally of the 3-level type. Room-temperature laser operation of $KYF_4:Er^{3+}$ and $LiYF_4:Er^{3+}$ was recently obtained in the green in pulsed operation with a flash-lamp-pumped Ti:sapphire laser as an ESA pump (Brede et al. 1993).

5.2.2. Anti-Stokes lasers in fluoride glass fibers

In fluoride glass fibers anti-Stokes lasers are favored for three reasons:

- (i) the existence of long-lived metastable states linked with the fluoride matrix;
- (ii) 3-level functioning linked with fiber optical confinement;
- (iii) the advantage of nonlinear pumping in an optically confined medium.

Since the first demonstration in 1986 (Mears et al. 1986) of the feasibility of CW room-temperature 3-level R lasers in Er^{3+} -doped glass fibers, one could think that an up-conversion pumped 3-level scheme could also be lased in CW operation at room-temperature. This was demonstrated at CNET by Allain et al. (1990) in a level scheme



Fig. 46. Energy scheme of the first CW room-temperature up-conversion laser (after Allain et al. 1990).

of the Ho^{3+} -doped fluoride fiber laser (fig. 46). Because of the weak Ho^{3+} concentration (1200 ppm) it was believed that within the single-ion-levels system ESA was taking place. However, since clustering may sometimes occur at much lower concentration there is still some doubt about the pumping process, as in many of the following up-conversion pumping fiber lasers.

 Er^{3+} -doped glass fibers have also shown CW room-temperature 3-level laser emission at 0.54 µm when pumped at 0.801 µm (Whitley et al. 1991). Because the pumping wavelength is in the laser-diode range there was hope that a compact fiber laser could be obtained. This has been quite recently confirmed by the demonstration of an InGaAsdiode-pumped Er^{3+} :ZBLAN fiber laser providing 18 mW of green laser light with a modest length of 2.5 m (Piehler 1994).

Besides these 2-photon up-conversion pumped lasers, a 3-photon one has recently been demonstrated in a Tm^{3+} -doped fiber (Grubb et al. 1992). Pumping at 1.12 µm, a room-temperature CW laser emission is obtained at 480 nm with a differential slope efficiency of 18%, with the threshold at a rather low 30 mW.

 Pr^{3+} -doped fluoride fibers, because of their low phonon energy, have allowed anti-Stokes pumping lasers at blue, green and red wavelength in the same fiber laser medium, also in CW room-temperature conditions (Smart et al. 1991).

5.2.3. Up-conversion laser with multiphonon-assisted pumping scheme and photon avalanche

Besides pumping in the electronic R ion transitions, as shown above, up-conversion pumping could be attempted in multiphonon side band pumping with energy mismatch as large as 1000 cm^{-1} (see sect. 3.2) (Auzel and Chen 1994). This was effectively the case for a Tm³⁺ fluoride fiber laser pumped at $1.06 \,\mu\text{m}$ in a 3-photon ESA process and lasing at $1.47 \,\mu\text{m}$ (Komukai et al. 1992). The 4-level scheme laser provides at room-temperature CW oscillation with a differential efficiency of 27%.



Fig. 47. Summary for laser and amplifier wave length observed in silica and fluoride fibers (Ronarc'h 1991)

Finally, it is worth mentioning an up-conversion avalanche laser in LaCl₃:Pr³⁺ single crystals (Koch et al. 1990). A CW emission in a 4-level scheme is obtained at 644 nm through an up-conversion avalanche process (sect. 3.4.3), under 677 nm pumping which corresponds to ESA pumping for the second step and probably to multiphonon absorption for the first one, as recently observed for ASE emission at 850 nm in an ZBLAN: Er^{3+} fiber in an avalanche regime (Chen and Auzel 1994a,b).

At this point we would like to stress that the APTE process is very general though sometimes erroneously believed to be of the cooperative type. This is due to its intrinsic efficiency linked to energy diffusion and because phonon assisted energy transfer always insures an energy matching. It is very likely that the matrices considered have smaller phonon energy giving long-lived metastable levels in an R system. It has then a pervading nature as shown by the many studies that have been devoted to such effects in fluoride systems even in glass form (Yeh et al. 1987, Quimby et al. 1987). Unless precluded by a lack of diffusion this very general effect is enhanced at high concentration $(10^{19} \text{ cm}^{-3} \text{ for trivalent R ions})$, and more efficiently when the excitation is concentrated in space, time and spectral domains because of its nonlinear nature.

In a fiber, with confinement of energy, such nonlinear processes are enhanced, even the ones with lower efficiencies such as ESA within single ions. Because the active ion concentration in a fiber is rather low (70–2000 ppm), ESA is believed to explain many of the observed up-conversion processes. However in cases where clusters of doping ions exist, such an explanation should be reconsidered (Auzel et al. 1994a, Blixt et al. 1991).

Due to the large number of papers in the field of amplifiers and lasers with R-doped fibers, this review cannot be complete, and we have shown only important turning points. An abstract of all the observed laser and amplifier wavelengths is given by fig. 47 as extracted from Ronarc'h (1991).

F. AUZEL

5.3. *R*-doped semiconductors and single-mode semiconductor lasers by coupling to *R*-doped insulators

5.3.1. Semiconducting III–V compounds and elemental semiconductors doped with Er^{3+}

As early as 1965 we tried to dope GaAs directly in the melt with metallic thulium. This attempt was stopped because the equilibrium obtained after cooling was such that thulium, though being one of the smallest R ions, was found to precipitate between the grains of the pure GaAs domains, as demonstrated by an auto-gammagraphy of the neutron activated thulium. With the advent of new epitaxial techniques such as molecular beam epitaxy (MBE) and liquid phase epitaxy (LPE) as well as ion implantation into bulk semiconductors, new trials were recently performed showing interesting results.

Photoluminescence spectra for the $Er^{3+} {}^{4}F_{13/2} \rightarrow {}^{4}F_{15/2}$ transition around 1.54 µm were first obtained in Er^{3+} -implanted and annealed Si at 20 K as well as in GaAs, GaP, InP by Ennen et al. (1983). The shape of the concentration profile may be modified by the implantation energy and the initial dose. For a dose of $2 \times 10^{4} Er/cm^{2}$ a maximum concentration of 10^{19} cm^{-3} may be obtained in InP after annealing at 600°C (Favennec et al. 1987) for an average implantation range of $0.2 \,\mu\text{m}$. A maximum of photoluminescence intensity was obtained at $1.5 \,\mu\text{m}$ for an Er^{3+} concentration in the average range of 10^{18} cm^{-3} (Rochaix et al. 1988). Besides implantation, direct Er^{3+} -doping was attempted during preparation of MBE layers (Charasse et al. 1988, Ennen et al. 1987). Photoluminescence emissions at $1.54 \,\mu\text{m}$ were obtained at $4 \,\text{K}$ and at 300 K for GaAs, AlGaAs, and GaAs/AlGaAs quantum wells. An example of such a spectrum is shown in fig. 48.



Fig. 48. Photoluminescence spectrum of GaAs:Er (~10¹⁷ cm⁻³) MBE layer at 9 K.





Because of the large difference in ionic radii for Er^{3+} (0.88 Å) and for Ga^{3+} (0.62 Å), Er^{3+} is introduced with great difficulty into the lattice. This is reflected in the spontaneous precipitation observed in our first experiment, though Tm^{3+} (0.869 Å) is somewhat smaller than Er^{3+} . We think it is also reflected by the R site observed in MBE GaAs: Er^{3+} samples as revealed by the energy level scheme (fig. 49). The number of Stark levels obtained by comparing excitation and photoluminescence spectra shows that the site symmetry is lower than cubic and may be orthorhombic (C_{2v}) (Ennen et al. 1987).

Interestingly, the magnitude of the crystal field as measured by the maximum Stark splitting of ${}^{4}F_{13/2}$ ($\Delta E_{max} = 353 \text{ cm}^{-1}$) (Auzel 1984b), is at least as large as in an ionic compound, e.g. for LaF₃ ($\Delta E_{max} = 219 \text{ cm}^{-1}$) (Auzel and Malta 1983). On the other hand, when Co²⁺ is incorporated into GaAs, the site crystal field (Dq $\approx 425 \text{ cm}^{-1}$) (Kaufman et al. 1982) is smaller than in small crystal field ionic compounds (Dq = 515 cm⁻¹ in KZnF₃) (Auzel 1987). These facts prompted the belief that Er³⁺ is incorporated in GaAs together with some impurity leading to ionic bonding with Er³⁺-like oxygen (Auzel 1988, 1989, Auzel et al. 1989b). It was suggested that deliberately introducing such ionic complexes could be the best way to dope III–V compounds (Auzel 1988, 1989), provided the electric properties of the pure crystal are not degraded too much.

5.3.2. Low-field electroluminescence

Although introducing Er^{3+} into GaAs still presents metallurgical difficulties, a very interesting result has been obtained: the low-field electroluminescence of Er^{3+} under direct current injection in a GaAs diode (Rolland et al. 1988). Figure 50 shows the diode structure, and fig. 51 the emission spectra, showing both the band-edge emissions at 0.83 µm at 77 K, 0.91 µm at 300 K and the Er^{3+} emission at 1.54 µm. It is interesting to note that at a current density lower than 80 A/cm², the 1.54 µm emission is larger than the band-edge one.

F. AUZEL



Fig. 50. GaAs:Er³⁺ diode structure for the low-field electroluminescence (from Rolland et al. 1988).

Fig. 51. Electroluminescence spectra of GaAs:Er diode (from Rolland et al. 1988).

The observed low-field excitation described here is very different from the impact excitation process in classical Destriau-type high-field electroluminescent systems (ZnS type). This has been recently investigated in detail (Lambert et al. 1990, Lhomer et al. 1991), (Benyattou et al. 1991, Seghier 1992). The R ion, in this case Yb^{3+} or Er^{3+} , acts as a trap for an excitation which transfers to the R ion by means of energy transfer according to the energy scheme of fig. 52a. In a semiconductor host, R ions suffer a special type of non-radiative decay not described in sect. 3, the "Auger effect" described by Langer (1988), which is in fact an APTE-like effect between the R ion as a sensitizer and the electron trap as an activator excited into non-radiative states of the host conduction band (fig. 52b).





Fig. 52. Excitation and non-radiative processes in InP:Yb (from Seghier 1992).

5.3.3. Er^{3+} and GaInAsP lasers for single-mode emission at 1.5 μ m

Doping a GaInAsP diode active layer with Er^{3+} by liquid phase epitaxy (LPE), Tsang and Logan (1986) have obtained, for the first time, a laser action on the ${}^{4}F_{13/2} \rightarrow {}^{4}F_{15/2}$ Er^{3+} transition by direct pulsed electric excitation of the diode at room temperature. The single-mode behavior on the Er^{3+} wavelength was attributed to the interaction between the band-edge gain profile and the Er^{3+} emission. Above 1.7 times the threshold current, emission would however also sometimes take place on band-edge emission. For one diode, single-mode emission at $1.532 \,\mu$ m has been obtained up to 10 times threshold instead of the $1.55 \,\mu$ m corresponding to the quaternary band-gap. The Rejection Mode Ratio (RMR) of other modes was about 13 dB. Another advantages of such a system, besides emission purity, was the high thermal stability of the wavelength: the respective coefficients being 1 Å/d° instead of $6.5 \,\text{Å/d°}$ on band-gap emission.

However, it appeared that single-frequency emission could be obtained sometimes at frequencies different from those of the Er^{3+} transitions; this was due to mode selection of band-gap emission through the precipitation of erbium-linked defects along the cavity length which then behave as a cut multi-cavity system selecting one mode in the semiconductor gain shape (Van der Ziel et al. 1987). Such precipitations are known to appear in R-doped semiconductors because of the difficulty in introducing the R within the semiconductor lattice (Nakagome et al. 1987). This difficulty is confirmed by the fact that introducing the R with some oxygen increases its efficiency (Favennec et al. 1990,



Fig. 53. Experiment for mode selection of an InGaAsP laser by Er^{3+} absorption (Zhou and Auzel 1993).

Adler et al. 1992); this fact also confirms the hypothesis that R in some cases (Er^{3+}) enters readily with oxygen impurities (Auzel 1988).

On the other hand, the oscillator strength for Yb³⁺ in InP ($f = 3 \times 10^{-6}$) was found to be about the same as in any other host (Auzel et al. 1989b), so the gain increase due to a R ion concentration of 10^{19} cm⁻³ can only be marginal ($10^{-1}-10^{-2}$ cm⁻¹) with respect to the semiconductor gain (~100 cm⁻¹); consequently the Tsang and Logan (1986) hypothesis was not tenable. In fact, negative gain (absorption) of about 100 cm⁻¹ can be obtained with R by using stoichiometric R materials, with a concentration level of 10^{21} cm⁻³. With an active length of about 200 µm, mode selection by Er³⁺ absorption has been obtained (Zhou and Auzel 1993) in the experimental configuration of fig. 53, providing a RMR of 35 dB (see fig. 54). In such an experiment, mode selection is provided by the Er³⁺ absorption transitions and not by a Fabry–Perot modulation; this allows the selected mode



Fig. 54. Emission spectrum of an InGaAsP laser (a) without and (b) with a LiYF₄: Er^{3+} 25%/ECMYAG combination (1 mm/216 µm) inside the laser cavity (Zhou and Auzel 1993).

to have a frequency fixed in an absolute way by the Er^{3+} . So, unless the concentration reaches the 10^{21} cm⁻³ level, coherent sources based on semiconductors doped with R are not likely to exist except with a very long active region (of the order of several mm).

However, R-doped semiconductors have evolved into a whole new field due mainly to the hope of obtaining silicon-based optoelectronic devices (Polman et al. 1993), that is, even using an indirect-gap semiconductor with no active optical property of its own. This field has been recently reviewed by Pomrenke et al. (1993).

6. Concluding remarks and hints for future trends

Having reviewed most of the basic processes which are involved in coherent sources with R ions, as well as key results and turning points for practical realization, we would like to conclude in an inductive way, trying to predict future trends from recent results and basic knowledge.

Most of the revival in this field in the late eighties is due to two factors: the recent advent of powerful and efficient monochromatic pumping sources provided by quantumwell semiconductor lasers; and the confinement obtained by a R-doped light-guiding active medium. This is the basis for the rapid development of R-doped fibers, new sources allowing, in particular, a 3-level CW laser scheme.

In another direction, the up-conversion pumping scheme, either of APTE or or ESA type, has evolved, allowing even CW laser UV sources at $381 \text{ nm} ({}^{4}D_{3/2} \rightarrow {}^{4}I_{11/2} \text{ transition of Nd}^{3+})$ at room temperature (Funk et al. 1994).

As for a crystalline host, the concept of a microchip (Zayhowski and Mooradian 1989) and stoichiometric laser is also revived by laser-diode pumping: crystalline materials even grown in very small volume can be used. One can easily predict that this opens the door to a large number of new laser hosts derived from the long studied field of crystalline powder phosphor materials recently reviewed by Blasse and Grabmaier (1994). Along the same lines new materials can be considered; for example, lower-energy phonon glasses for new transitions (Hewak et al. 1994), or composite materials such as glass ceramics (Auzel et al. 1975, Wang and Ohwaki 1993, Santa-Cruz et al. 1994).

From the diode-pumped fiber scheme, the new field of confined-medium systems is evolving into the R-doped planar waveguide amplifier and laser system. A preliminary result was a Nd³⁺-doped lithium niobate optical waveguide (Li et al. 1988), rapidly followed by the laser action itself (Lallier et al. 1989, Haruna et al. 1994), thus opening the way to Er^{3+} -doped silica-based planar waveguides on silicon substrate (Kitagawa et al. 1991). However, for a gain of 9.4 dB at 1.5 µm, an S-shape length of 21 cm is still necessitated by the small amount of R which can be introduced (3800 ppm) (Hattori et al. 1993). Laser action has been obtained in a vapor-deposited Er^{3+} -doped glass waveguide of 6.5 cm length doped at a 500 ppm level (Nakazawa and Kimura 1992). Such waveguide amplifiers and lasers could compete with doped fibers only if the length would be much smaller; such is the case for crystalline waveguides for which R has a larger cross-section. Gains of 5 dB have been obtained in $Er:Y_2O_3$ guides with 2.8 cm length (Horst et al. 1994). Besides this, we can imagine that epitaxial growth of R-doped wave guide structure would open the way to future monolithic structures, including semiconductor pumping and a R-doped waveguide. Results from both the R and the semiconductor sides are coming in sight. On the one hand very efficient epitaxial waveguide lasers have been obtained: Nd^{3+} :YAG, Yb^{3+} :YAG, and Yb^{3+} :Er³⁺:YAG (Chartier et al. 1992, Pelenc et al. 1993, Sheperd et al. 1994); on the other hand, epitaxial growth of CaF₂:Er³⁺ layers has been obtained on Si (Barrière et al. 1993). One can anticipate that a common substrate could be used to grow both semiconductor and R active layers. Besides the development of guiding layers, photo-imprinted gratings are being used as reflecting mirrors for waveguide lasers (Kitagawa et al. 1994), and for fiber lasers (Ball et al. 1991, Zyskind et al. 1992). All these features are premonitory indications of possible future R-doped active optical monolytic circuits.

Returning to the beginning of sect. 2, one can note that most of the practical laser coherent sources or amplifiers with R ions do not make full use of the direct coherent exchange between the atom and field at times shorter than T_2 . Directions towards control of such a basic process can be found in efforts to reduce the dimensionality of the active cavity by reducing its size to less than a wavelength (for example, in microcavities (Schubert et al. 1993), or in coupling R ions to sub-nanosize metal dots (Malta et al. 1985), or recently in metallized thinned doped fibers (Brorson and Skovgaard 1994). All these directions allow great expectations for new applications of the coherent properties of R ions.

Acknowledgements

I am very grateful to Josette Chavignon for patiently and efficiently typing the manuscript over several months, and to Fabienne Pellé for carefully reading and correcting the manuscript. Many thanks are due to Daniel Meichenin, my faithful collaborator in the laboratory for more than twenty years; without him many original results presented here would not exist. Finally, I am indebted to Rino DiBartolo for having invited me to lecture many times at his *Summer School On Spectroscopy* in Erice (Italy) and thus forced me to deepen many aspects of the fields presented here.

References

- Adler, D.L., D.C. Jacobson, D.J. Eaglesham, M.A. Marcus, J.L. Brenton, J.M. Poate and P.H. Citrin, 1992, Appl. Phys. Lett. 61, 2181.
- Allain, J.Y., M. Monerie and H. Poignant, 1989, Electron. Lett. 25, 318.
- Allain, J.Y., M. Monerie and H. Poignant, 1990, Electron. Lett. 26, 261.
- Allen, H., and J.H. Eberly, 1975, Optical Resonance and Two-Level Atoms (Wiley, New York).
- Arrechi, F.T., and E. Courtens, 1970, Phys. Rev. A 2, 1730.
- Asawa, C.K., and M. Robinson, 1966, Phys. Rev. 141, 251.
- Auzel, F., 1966a, C.R. Acad. Sci. 263, 765.

- Auzel, F., 1966b, C.R. Acad. Sci. **262**, 1016; **263**, 819.
- Auzel, F., 1968, Contribution à l'Etude Spectroscopique de Verres Dopés avec Er³⁺ pour Obtenir l'Effet Laser, Thèse (Université de Paris).
- Auzel, F., 1969a, Ann. Télécom. (Paris) 24, 363.
- Auzel, F., 1969b, Ann. Télécom. (Paris) 24, 199.
- Auzel, F., 1973, Proc. IEEE 61, 758.
- Auzel, F., 1976, Phys. Rev. B 13, 2809.
- Auzel, F., 1978, Multiphonon interaction of excited luminescent centers in the weak coupling limit: non-radiative decay and multiphonon sidebands, in: Luminescence of Inorganic Solids, ed. B. Di Bartolo (Plenum Press, New York) p. 67.
- Auzel, F., 1979, Mat. Res. Bull. 14, 223.
- Auzel, F., 1980a, Multiphonon processes, crossrelaxation and up-conversion in ion-activated solids, exemplified by minilaser materials, in: Radiationless Processes, eds B. Di Bartolo and V. Goldberg (Plenum Press, New York) p. 213.
- Auzel, F., 1980b, The Rare-Earths in Modern Science and Technology, Vol. 2, eds G.J. McCarthy, J.J. Rhyne and H.B. Silber (Plenum Press, New York) p. 619.
- Auzel, F., 1980c, in: Processes in Heavily Doped Rare-Earth Materials and their Applications to Semiconductor Optoelectronics, ed. M.A. Herman (PWN, Polish Scientific Publishers/Wiley, Warsaw/ New York) p. 233.
- Auzel, F., 1984a, J. Lumin. 31/32, 759.
- Auzel, F., 1984b, A scalar crystal field parameter for rare earth ions: meaning and application to energy transfers, in: Energy Transfers Processes in Condensed Matter, ed. B. Di Bartolo (Plenum Press, New York) p. 511.
- Auzel, F., 1985, Rare-Earth Spectroscopy, eds B. Trzebiatowska, J. Legendziewicz and W. Stręk (World Scientific, Singapore) p. 502.
- Auzel, F., 1987, Materials for Ionic Solid State Lasers, in Spectroscopy of Solid State Laser-type Materials, ed. B. Di Bartolo (Plenum Press, New York) p. 293.
- Auzel, F., 1988, Will Er³⁺ become as useful as Nd³⁺ in new solid state laser materials?, French-Israeli Workshop on Solid State Lasers, 12–14 Dec., Jerusalem.
- Auzel, F., 1989, Proc. SPIE 1182, 59.
- Auzel, F., 1990, J. Lumin. 45, 341.
- Auzel, F., 1991, Advances in non-radiative processes in solid state laser materials, in: Advances in Non-

Radiative Processes in Solids, ed. B. Di Bartolo (Plenum Press, New York) p. 135.

- Auzel, F., 1992, Properties of highly populated excited states in solids: superfluorescence, hot luminescence, excited state absorption, in: Optical Properties of Excited States in Solids, ed. B. Di Bartolo (Plenum Press, New York) p. 305.
- Auzel, F., 1993, Amplifiers and lasers with optical fibres, in: Defects in Insulating Materials, ed. O. Kanert and J.M. Spaeth (World Scientific, Singapore) p. 39.
- Auzel, F., and Y.H. Chen, 1994, J. Lumin. 60/61, 101.
- Auzel, F., and Y.H. Chen, 1995, J. Lumin. 65, 45.
- Auzel, F., and O.K. Deutschbein, 1969, Z. Naturforsch. 24a, 1562.
- Auzel, F., and O.L. Malta, 1983, J. Phys. 44, 201.
- Auzel, F., and J.C. Michel, 1975, C.R. Acad. Sci. Ser. B 279, 187.
- Auzel, F., and D. Pécile, 1973, C.R. Acad. Sci. Ser. B 277, 155.
- Auzel, F., D. Pécile and D. Morin, 1975, J. Electrochem. Soc. 122, 101.
- Auzel, F., J. Dexpert-Ghys and C. Gautier, 1982, J. Lumin. 27, 1.
- Auzel, F., S. Hubert and D. Meichenin, 1988a, Europhys. Lett. 7, 459.
- Auzel, F., D. Meichenin and H. Poignant, 1988b, Electron. Lett. 24, 1463.
- Auzel, F., S. Hubert and D. Meichenin, 1989a, Appl. Phys. Lett. 54, 681.
- Auzel, F., A.M. Jean-Louis and Y. Toudic, 1989b, J. Appl. Phys. 66, 3952.
- Auzel, F., J. Chavignon, D. Meichenin and M. Poulain, 1993, J. Non-Cryst. Solids 161, 109.
- Auzel, F., D. Meichenin, F. Pellé and P. Goldner, 1994a, Opt. Mat. 4, 35.
- Auzel, F., Y.H. Chen and D. Meichenin, 1994b, J. Lumin. 60/61, 692.
- Axe, J.D., and P.F. Weller, 1964, J. Chem. Phys. 40, 3066.
- Ball, G.A., W.W. Morey and W.H. Glenn, 1991, IEEE Trans. Photonics Technol. Lett. 3, 613.
- Barrière, A.S., B. Mombelli, B. Porté, S. Raoux, H. Guégan, M. Réan, H. L'Haridon and D. Moutonnet, 1993, J. Appl. Phys. 73, 1180.
- Becker, P.C., J.R. Simpson and N. Olsson, 1996, Erbium Fibre Amplifiers, Fundamentals and Technology (Academic Press, New York).
- Benyattou, T., D. Seghier, G. Guillot, R. Mongorgé, P. Galtier and M.N. Charasse, 1991, Appl. Phys. Lett. 58, 2132.

- Blasse, G., and B.C. Grabmaier, 1994, Luminescent Materials (Springer, Berlin).
- Blixt, P., J. Nilsson, J. Carlnäs and B. Jaskorzynska, 1991, IEEE Trans. Phot. Technol. Lett. 3, 996.
- Boccara, A.C., 1987, Photoacoustic and photothermal characterization of laser material, in: Spectroscopy of Solid State Laser-type Materials, ed. B. Di Bartolo (Plenum Press, New York) p. 475.
- Boggis, J.M., A. Lord, W.A. Stallard and P. Cochrane, 1991, Electron. Lett. 27, 129.
- Bonifacio, R., and L.A. Lugiato, 1975, Phys. Rev. A 11, 1507.
- Bonneville, R., and F. Auzel, 1976, Opt. Commun. 18, 51.
- Brandel, V., G. Iroulart, E. Simoni and M. Genet, 1991, New J. Chem. 15, 247.
- Brede, R., E. Heumann, J. Koetke, T. Danger, G. Huber and B. Chai, 1993, Appl. Phys. Lett. 63, 2030.
- Brierley, M.C., and P.W. France, 1988, Electron. Lett. 24, 935.
- Brorson, S.D., and P.M.W. Skovgaard, 1994, in: Proc. EQEC'94, QW G-4.
- Budin, J.P., J.C. Michel and F. Auzel, 1979, J. Appl. Phys. 50, 641.
- Carlson, N.W., D.J. Jackson, A.L. Schawlow, M. Gross and S. Haroche, 1980, Opt. Commun. 32, 350.
- Carter, J.N., R.G. Smart, A.C. Tropper, D.C. Hanna, S.F. Carter and D. Szebesta, 1991, J. Lightwave Technol. 9, 1548.
- Case, W.E., M.E. Koch and A.W. Kueny, 1990, J. Lumin. 45, 351.
- Charasse, M.N., P. Galtier, F. Lemaire, J.P. Hirtz, A.M. Huber, C. Grattepain, O. Lagorsse, J. Chazelas, N. Vodjani and C. Weissbuch, 1988, Le Vide, Les Couches Minces 241, 185.
- Chartier, I., B. Ferrand, D. Pelenc, S.J. Field, D.C. Hanna, A.C. Large, D.P. Sheperd and A.C. Tropper, 1992, Opt. Lett. 17, 810.
- Chen, Y.H., and F. Auzel, 1994a, Electron. Lett. 30, 323.
- Chen, Y.H., and F. Auzel, 1994b, J. Phys. D 27, 1.
- Chen, Y.H., and F. Auzel, 1994c, Electron. Lett. 30, 1602.
- Chivian, J.S., W.E. Case and D.D. Eden, 1979, Appl. Phys. Lett. 35, 124.
- Chrysochoos, J., 1974, J. Chem. Phys. 61, 4596.
- Clescla, B., D. Ronarc'h, D. Bayart, Y. Sorel, L. Hamon, M. Guibert, J.L. Beylat, J.K. Kerdiles and M. Semenkoff, 1994a, IEEE Trans. Photon. Technol. Lett. 6, 509.

- Clescla, B., D. Bayart, L. Hamon, J.L. Beylat, C. Coeurjolly and L. Berthelou, 1994b, Electron. Lett. 30, 586.
- CNET Group, 1963, Research on Vitreous Laser Materials, in: Final Technical Report, Contract Nm. DA-91-591-EUC-2793 (US Dept. of Defense, Washington, DC) p. 3.
- Cockroft, N.J., G.D. Jones and R.W.G. Syme, 1989, J. Lumin. 43, 275.
- Cozannet, A., J. Fleuret, H. Maitre and M. Rousseau, 1981, Optique et Télécommunications (Eyrolle, Paris) p. 217.
- Danielmeyer, H.G., 1975, Advances in Lasers, Vol. IV (Marcel Dekker, New York).
- Danielmeyer, H.G., and H.P. Weber, 1972, IEEE J. Quantum Electron. 8, 805.
- De Loach, L.D., S.A. Payne, W.L. Kway, J.B. Tassano, S.N. Dixit and W.F. Krupke, 1994, J. Lumin. 62, 85.
- De Voe, R.G., and R.G. Brewer, 1983, Phys. Rev. Lett. 50, 1269.
- Desurvire, E., 1994, Erbium-doped Fibre Amplifiers: Principles and Applications (Wiley, New York).
- Desurvire, E., J.R. Simpson and P.C. Becker, 1987, Opt. Lett. 12, 888.
- Desurvire, E., C.R. Giles, J.R. Simpson and J.L. Zyskind, 1989, Opt. Lett. 14, 1266.
- Deutschbein, O.K., 1976, IEEE J. Quantum Electron. 12, 551.
- Deutschbein, O.K., and C. Pautrat, 1968, IEEE J. Quantum Electron. 4, 48.
- Deutschbein, O.K., C. Pautrat and F. Auzel, 1964, Etude PCM 727 (CNET) p. 15.
- Dexpert-Ghys, J., and F. Auzel, 1984, J. Chem. Phys. 80, 4003.
- Dexter, D.L., 1953, J. Chem. Phys. 21, 836.
- Di Bartolo, B., 1968, Optical Interactions in Solids (Wiley, New York).
- Dieke, R.H., 1954, Phys. Rev. 93, 99.
- Digonnet, M.J.F., 1993, Rare Earth Doped Fiber Lasers and Amplifiers (Marcel Dekker, New York).
- Edagawa, E., M. Suzuki, K. Mochizuki and H. Wakabayashi, 1989, in: Proc. IOOC'89, 18–21 July, Kobe, Japan, 21 B4-1.
- Engelman, R., 1979, Non-Radiative Decay of Ions and Molecules in Solids (North-Holland, Amsterdam).
- Ennen, H., J. Schneider, G.S. Pomrenke and A. Axmann, 1983, Appl. Phys. Lett. 43, 943.
- Ennen, H., J. Wagner, H.D. Müller and R.S. Smith, 1987, J. Appl. Phys. 61, 4877.

- Favennec, P.N., H. L'Haridon, A. Le Corre, M. Salvi and M. Gauneau, 1987, Electron. Lett. 23, 684.
- Favennec, P.N., H. L'Haridon, D. Moutonnet, M. Salvi and M. Gauneau, 1990, Jpn. J. Appl. Phys. 29, L524.
- Florian, R., L.O. Schwan and D. Schmid, 1982, Solid State Commun. 42, 55.
- Florian, R., L.O. Schwan and D. Schmid, 1984, Phys. Rev. A 29, 2709.
- Fong, F.K., 1975, Theory of Molecular Relaxation (Wiley, New York).
- Fong, F.K., 1979, Non-radiative processes of rareearth ions in crystals, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 4, ed. K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam) p. 317.
- Fong, F.K., S.L. Naberhuis and M.M. Miller, 1972, J. Chem. Phys. 56, 4020.
- Förster, T., 1948, Ann. Phys. 2, 55.
- Förster, T., 1960, Radiat. Res. Suppl. 2, 326.
- Fowler, W.B., W. Beall and D.L. Dexter, 1962, Phys. Rev. 128, 2154.
- Friedberg, R., and S.R. Hartmann, 1971, Phys. Lett. A 37, 285.
- Funk, D.S., J.W. Carlson and J.G. Eden, 1994, Electron. Lett. **30**, 1860.
- Gain Project, 1994, RACE GAIN R2018 Consortium leaflet, ECOC'94, 25–30 September, Firenze, Italy.
- Genack, A.Z., R.M. Macfarlane and R.G. Brewer, 1976, Phys. Rev. Lett. 37, 1078.
- Giles, C.R., E. Desurvire, J.L. Zyskind and J.R. Simpson, 1989, in: Proc. IOOC'89, Kobe, Japan, 18–21 July, 20PD15.
- Gomes, A.S.L., G.S. Maciel and C.B. de Araujo, 1993, Tech. Dig., ICL'93, Storrs, CN, USA, 9–12 August, Th 3C-3.
- Gouedard, C., D. Husson, C. Sauteret, F. Auzel and A. Migus, 1991, IAEA Conf. on Drivers for Inertial Confinement Fusion, Osaka, Japan, 15-19 April, Paper E04.
- Gouedard, C., D. Husson, C. Sauteret, F. Auzel and A. Migus, 1993, J. Opt. Soc. Am. B 10, 2358.
- Grant, W.J.C., 1958, Phys. Rev. 109, 648.
- Gross, M., and S. Haroche, 1982, Phys. Rep. 93, 301.
- Grubb, S.G., K.B. Bennett, R.S. Cannon and W.F. Humer, 1992, Electron. Lett. 28, 1243.
- Guggenheim, H.G., and L.F. Johnson, 1971, Appl. Phys. Lett. 19, 44.
- Haas, Y., and G. Stein, 1974, Chem. Phys. Lett. 11, 143.

- Haken, H., 1981, Light, Waves, Photons, Atoms, Vol. 1 (North-Holland, Amsterdam).
- Haruna, M., H. Sewai, H. Nishihara, S. Ikunishi, T. Gozen and H. Tanaka, 1994, Electron. Lett. 30, 412.
- Hattori, K., T. Kitagawa, M. Oguma, M. Wada, J. Temmyo and M. Horiguchi, 1993, Electron. Lett. 29, 357.
- Hebert, T., R. Wannemacher, W. Lenth and R.M. Macfarlane, 1990, Appl. Phys. Lett. 57, 1727.
- Hebert, T., R. Wannemacher, R.M. Macfarlane and W. Lenth, 1992, Appl. Phys. Lett. 60, 2592.
- Hewak, D.W., B.N. Samson, J.A. Medeiros Neto, R.J. Laming and D.N. Payne, 1994, Electron. Lett. 30, 968.
- Hill, R.M., D.E. Kaplan, G.F. Herrmann and S.K. Ichiki, 1967, Phys. Rev. Lett. 18, 105.
- Hong, H.Y., and S.R. Chinn, 1976, Mater. Res. Bull. 11, 421.
- Horst, F., T.H. Hoekstra, P.V. Lambeck and T.J.A. Popma, 1994, Opt. Quantum Electron. 26, S285.
- Huang, K., and A. Rhys, 1950, Proc. R. Soc. London Ser. A 204, 406.
- Hubert, S., D. Meichenin and F. Auzel, 1990, J. Lumin. **45**, 434.
- Inokuti, M., and F. Hirayama, 1965, J. Chem. Phys. 43, 1978.
- Jaynes, E.T., and F.W. Cummings, 1963, Proc. IEEE 51, 89.
- Johnson, L.F., and H.J. Guggenheim, 1974, IEEE J. Quantum Electron. 10, 442.
- Johnson, L.F., and K. Nassau, 1961, Proc. IRE 49, 1704.
- Johnson, L.F., R.E. Dietz and H.J. Guggenheim, 1963, Phys. Rev. Lett. 11, 318.
- Joubert, M.F., S. Guy and B. Jacquier, 1993, Phys. Rev. B 46, 10031.
- Judd, B.R., 1962, Phys. Rev. 127, 750.
- Judd, B.R., 1988, Atomic theory and optical spectroscopy, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 11, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam) p. 135.
- Kaiser, W., C.G.B. Garrett and D.L. Wood, 1961, Phys. Rev. 123, 766.
- Kaminskii, A.A., 1978, Topical problems of laser crystal physics, in: Luminescence of Inorganic Solids, ed. B. Di Bartolo (Plenum Press, New York) p. 511.
- Kaminskii, A.A., 1981, Laser Crystals (Springer, Berlin).
- Kaufman, U., H. Ennen, J. Schneider, R. Wörmer, J. Weller and F. Köhl, 1982, Phys. Rev. B 25, 5598.
- Kiel, A., 1964, Multiphonon spontaneous emission in paramagnetic crystals, in: Quantum Electronics, eds P. Grivet and N. Bloembergen (Dunod, Paris) p. 765.
- Kintz, G.J., R. Allen and L. Esterowitz, 1987, Appl. Phys. Lett. 50, 1553.
- Kitagawa, T., K. Hattori, M. Shimizu, Y. Omori and M. Kobayashi, 1991, Electron. Lett. 27, 334.
- Kitagawa, T., F. Bilsdean, B. Malo, S. Thérianet, J. Albert, D.C. Johnson, K.O. Hill, K. Hattori and Y. Hibino, 1994, Electron. Lett. 30, 1311.
- Kittel, C., 1971, Introduction to Solid State Physics (Wiley, New York) p. 201.
- Klemens, P.G., 1958, Solid State Physics, Vol. 7, eds F. Seitz and D. Turnbull (Academic Press, New York) p. 1.
- Koch, M.E., A.W. Kueny and W.E. Case, 1990, Appl. Phys. Lett. 56, 1083.
- Komukai, T., T. Yamamoto, T. Sugawa and Y. Miyajima, 1992, Electron. Lett. 28, 830.
- Krasutsky, N.J., 1983, J. Appl. Phys. 54, 1261.
- Kueny, A.W., W.E. Case and M.E. Koch, 1989, J. Opt. Soc. Am. B 6, 639.
- Kuhn, H.G., 1962, Atomic Spectra (Longmans, London) p. 390.
- Kurnit, N.A., I.D. Abella and S.R. Hartmann, 1964, Phys. Rev. Lett. 13, 567.
- Kushida, T., 1969, Phys. Rev. 185, 500.
- Kushida, T., 1973, J. Phys. Soc. Jpn. 34, 1318.
- Kustov, E.F., T.K. Maketov, G. Streczo and A.K. Projevudsky, 1980, Phys. Status Solidi A 60, 225.
- Lallier, E., J.P. Pocholle, M. Papuchon, C. Grezes-Besset, E. Pelletier, M. de Micheli, M.J. Li, Q. He and D.B. Ostrowsky, 1989, Electron. Lett. 25, 1491.
- Lambert, B., A. Le Corre, Y. Toudic, C. Lhomer, G. Grandpierre and M. Gauneau, 1990, J. Phys.: Condens. Matter 2, 479.
- Langer, J.M., 1988, J. Lumin. 40/41, 589.
- Lauder, R.D.T., J.N. Carter, D.C. Hanna, A.C. Tropper, H.M. Pask, S.T. Davey and D. Szebesta, 1993, J. Non-Cryst. Solids 161, 274.
- Leibfried, G., and E. Schloemann, 1954, Nachr. Akad. Wiss. Göttingen Math.-Phys. KI. 2A: Math. Phys. Chem. Abt., p. 71.
- Lempicki, A., and H. Samelson, 1963, Phys. Lett. 4, 133.
- Lenth, W., and R.M. Macfarlane, 1990, J. Lumin. 45, 346.

- Lhomer, C., B. Lambert, Y. Toudic, A. Le Corre, M. Gauneau, F. Clerot and B. Sermage, 1991, Semicond. Sci. Technol. 6, 916.
- Li, M.J., M.P. de Micheli, D.B. Ostrowsky, E. Lallier, J.M. Breteau, M. Papuchon and J.P. Pocholle, 1988, Electron. Lett. 24, 914.
- Lin, G.K., M.F. Joubert, R.L. Cone and B. Jacquier, 1987, J. Lumin. 38, 34.
- Macfarlane, R.M., 1992, Laser spectroscopy inside inhomogeneously broadened lines, in: Optical Properties of Excited States in Solids, ed. B. Di Bartolo (Plenum Press, New York) p. 399.
- Macfarlane, R.M., and R.M. Shelby, 1982, Opt. Commun. 42, 346.
- Macfarlane, R.M., and R.M. Shelby, 1987, Coherent transient and holeburning spectroscopy of rare-earth ions in solids, in: Spectroscopy of Solids Containing Rare-Earth Ions, eds A.A. Kaplyanski and R.M. Macfarlane (North-Holland, Amsterdam) p. 51.
- Macfarlane, R.M., C.S. Yannoni and R.M. Shelby, 1980, Opt. Commun. **32**, 101.
- Macfarlane, R.M., F. Tong, A.J. Silversmith and W. Lenth, 1988, Appl. Phys. Lett. 12, 1300.
- MacGillivray, J.C., and M.S. Feld, 1976, Phys. Rev. A 14, 1169.
- Maiman, T.H., 1960, Nature 187, 493.
- Malcuit, M.S., J.J. Maki, D.J. Simkin and R.W. Boyd, 1987, Phys. Rev. Lett. **59**, 1189.
- Malikov, R.F., and E.D. Trifonov, 1984, Opt. Commun. 52, 74.
- Malta, O.L., P.A. Santa-Cruz, G.F. de Sá and F. Auzel, 1985, J. Lumin. 33, 261.
- Marcerou, J.F., S. Artigaud, J. Hervo and H. Fevrier, 1992, Tech. Digest, ECOC'92, Berlin, No. 12-Y.
- Markushev, V.M., V.F. Zolin and C.M. Briskina, 1986, Sov. J. Quantum Electron. 16, 281.
- Mears, R.J., L. Reekie, S.B. Poole and D.N. Payne, 1986, Electron. Lett. 22, 159.
- Mears, R.J., L. Reekie, J.M. Jauncey and D.N. Payne, 1987, Electron. Lett. 23, 1026.
- Melamed, N.J., 1963, J. Appl. Phys. 34, 560.
- Michel, J.C., D. Morin and F. Auzel, 1978, Rev. Phys. Appl. 13, 859.
- Miller, R.C., 1964, Appl. Phys. Lett. 5, 17.
- Miyajima, Y., T. Sugawa and Y. Fukasaku, 1991, Electron. Lett. 27, 1706.
- Miyakawa, T., 1973, in: Luminescence of Crystals, Molecules and Solutions, ed. F. Williams (Plenum Press, New York) p. 394.
- Miyakawa, T., and D.L. Dexter, 1971, Phys. Rev. B 1, 70.

- Müller, G., and N. Neuroth, 1973, J. Appl. Phys. 44, 2315.
- Nakagome, H., K. Takahei and Y. Homma, 1987, J. Cryst. Growth 85, 345.
- Nakazawa, E., and S. Shionoya, 1970, Phys. Rev. Lett. 25, 1710.
- Nakazawa, M., and Y. Kimura, 1992, Electron. Lett. 28, 2054.
- Ni, H., and S.C. Rand, 1991, Opt. Lett. 16, 1424.
- Ni, H., and S.C. Rand, 1992, Opt. Lett. 17, 1222.
- Oetliker, U., M.J. Riley, P.S. May and H.U. Güdel, 1992, J. Lumin. 53, 553.
- Olskansky, R., 1988, Electron. Lett. 24, 1365.
- Orbach, R., 1975, in: Optical Properties of Ions in Solids, ed. B. Di Bartolo (Plenum Press, New York) p. 445.
- Ovsyankin, V.V., 1987, Spectroscopy of collective states and cooperative transitions in disordered rareearth activated solids, in: Spectroscopy of Solids Containing Rare-Earth Ions, eds A.A. Kaplyanskii and R.M. Macfarlane (North-Holland, Amsterdam) p. 405.
- Ovsyankin, V.V., and A.A. Fedorov, 1981, Opt. Spectros. (USSR) 50, 565.
- Ovsyankin, V.V., and P.P. Feofilov, 1966, Sov. Phys. JEPT Lett. 4, 317.
- Pelenc, D., B. Chambaz, I. Chartier, B. Ferrand, D.C. Hanna and D.P. Sheperd, 1993, in: Proc. European Conf. on Integrated Optics, C.S.E.M., Neuchâtel, Switzerland, pp. 3–8.
- Pellé, F., and P. Goldner, 1993, Phys. Rev. B 48, 9995.
- Pelletier-Allard, N., and R. Pelletier, 1987, Phys. Rev. B 26, 4425.
- Percival, R.M., D. Szebesta, J.R. Williams, R.D.T. Lauder, A.C. Tropper and D.C. Hanna, 1994, Electron. Lett. 30, 1598.
- Peterson, G.E., and P.M. Bridenbaugh, 1964, J. Opt. Soc. Am. 54, 644.
- Piehler, D., 1994, in: Proc. IEEE/LEOS annual meeting, Boston, 3 Nov., 556.1.
- Polder, D., M.F.H. Schuurmans and Q.H.F. Vrehen, 1979, Phys. Rev. A 19, 1192.
- Polman, A., J.S. Custer, E. Snoeks and G.N. Van den Hoven, 1993, Appl. Phys. Lett. 62, 507.
- Pomrenke, G.S., P.B. Klein and D.W. Langer, eds, 1993, Rare Earth Doped Semiconductors, MRS Symp. 301.
- Pouradier, J.F., and F. Auzel, 1978, J. Phys. 39, 825.
- Quimby, R.S., M.G. Drexhage and M.J. Suscavage, 1987, Electron. Lett. 23, 33.

- Reekie, L., J.M. Jauncey, S.B. Poole and D.N. Payne, 1987, Electron. Lett. 23, 1076.
- Reisfeld, R., and C.K. Jørgensen, 1977, Lasers and Excited States of Rare-Earths (Springer, Berlin).
- Rios Leite, J.R., and C.B. de Araujo, 1980, Chem. Phys. Lett. 73, 71.
- Riseberg, L.A., and H.W. Moos, 1968, Phys. Rev. 174, 429.
- Rochaix, C., A. Rolland, P.N. Favennec, B. Lambert, H. Le Corre, H. L'Haridon and M. Salvi, 1988, J. Electron. Mat. 17, 351.
- Roess, D., 1969, Laser Light Amplifiers and Oscillators (Academic Press, New York).
- Rolland, A., A. Le Corre, P.N. Favennec, M. Gauneau, B. Lambert, D. Lecronier, H. L'Haridon, D. Moutonnet and C. Rochaix, 1988, Electron. Lett. 24, 957.
- Ronarc'h, D., 1991, Echo Rech. 143, 75.
- Ronarc'h, D., M. Guibert, F. Auzel, D. Meichenin, J.Y. Allain and H. Poignant, 1991a, Electron. Lett. 27, 511.
- Ronarc'h, D., M. Guibert, H. Ibrahim, M. Monerie, H. Poignant and A. Tromeur, 1991b, Electron. Lett. 27, 908.
- Santa-Cruz, P.A., D. Morin, J. Dexpert-Ghys, A. Sadoc, F. Glas and F. Auzel, 1994, in: Proc. 9th ISNOG Conf., Hangzhou, China, May 25–27, 28-AM, A8, 400.
- Santa-Cruz, P.A., D. Morin, J. Dexpert-Ghys, A. Sadoc, F. Glas and F. Auzel, 1995, J. Non-Cryst. Solids 190, 238.
- Schiller, A., L.O. Schwan and D. Schmid, 1987, J. Lumin. 38, 243.
- Schubert, E.F., N.E.J. Hunt, A.M. Vredenberg, T.D. Harris, J.M. Poate, D.C. Jacobson, Y.H. Wong and G.J. Zydzik, 1993, Appl. Phys. Lett. 63, 2603.
- Schuurmans, M.F.H., 1980, Opt. Commun. 34, 185.
- Schuurmans, M.F.H., and D. Polder, 1979, Phys. Lett. A 72, 306.
- Schwan, L.O., 1991, J. Lumin. 48/49, 289.
- Scott, B.P., F. Zhao, R.S.F. Chang and N. Djeu, 1993, Opt. Lett. 18, 113.
- Seghier, D., 1992, Etude des propriétés optiques et électriques des matériaux semi-conducteurs III–V dopés aux ions terres rares en vue de la réalisation de dispositifs électroluminescents, Thèse (INSA, Lyon, France).
- Shelby, R.M., and R.M. Macfarlane, 1984, J. Lumin. 31/32, 839.
- Sheperd, D.P., D.C. Hanna, A.C. Large, A.C. Tropper, T.J. Warbuton, C. Borel, B. Ferrand, D. Pelenc, A.

Rameix, P. Thony, F. Auzel and D. Meichenin, 1994, J. Appl. Phys. 76, 7651.

- Singh, S., D.C. Miller, J.R. Potopowicz and L.K. Shick, 1975a, J. Appl. Phys. 46, 1191.
- Singh, S., R.B. Chesler, W.H. Grodkiewicz, J.R. Potopowicz and L.G. Van Uitert, 1975b, J. Appl. Phys. 46, 436.
- Skribanowitz, N., I.P. Herman, J.C. MacGillivray and M.S. Feld, 1973, Phys. Rev. Lett. 30, 309.
- Smart, R.G., D.C. Hanna, A.C. Tropper, S.T. Davey, S.F. Carter and D. Szebesta, 1991, Electron. Lett. 27, 1308.
- Snitzer, E., 1961, Phys. Rev. Lett. 7, 444.
- Snitzer, E., and R. Woodcock, 1965, Appl. Phys. Lett. 6, 45.
- Sorokin, P.R., M.J. Stevenson, J.R. Lankard and G.D. Pettit, 1962, Phys. Rev. 127, 503.
- Stavola, M., and D.L. Dexter, 1979, Phys. Rev. B 20, 1867.
- Stenholm, S., 1973, Phys. Rep. 6, 1.
- Stephens, R.R., and R.A. Macfarlane, 1993, Opt. Lett. 18, 34.
- Stokowski, S.E., R.A. Saroyan and M.J. Weber, 1978, Nd-doped Laser Glass, Spectroscopic and Physical Properties (Lawrence Livermore Laboratory, Livermore, CA, USA).
- Stone, J., and C.A. Burrus, 1974, Appl. Opt. 13, 1256.
- Strek, W., C. Szafranski, E. Lukowiak, Z. Mazurak and B. Jerowska, 1977, Phys. Status Solidi 41, 547.
- Struck, C.W., and W.H. Fonger, 1991, Radiative and non-radiative rates in luminescence centers, in: Advances in Non-Radiative Processes in Solids, ed. B. Di Bartolo (Plenum Press, New York) p. 63.
- Sunak, H.R.D., 1991, Bibliography on Erbium Doped Fibre Amplifiers: 1987 to 1990 (EDFA Consultants).
- Tofield, B.C., and H.P. Weber, 1974, Phys. Rev. B 10, 4560.
- Tong, F., W.P. Risk, R.M. Macfarlane and W. Lenth, 1989, Electron. Lett. 25, 1389.
- Toyozawa, T., 1967, in: Dynamical Processes in Solid State Optics, ed. R. Kubo (Benjamin, New York) p. 90.
- Tsang, W.T., and R.A. Logan, 1986, Appl. Phys. Lett. 49, 1686.
- Vagin, Y.S., V.M. Marchenko and A.M. Prokhorov, 1968, Zh. Eksp. Teor. Fiz. 55, 1717.
- Van der Ziel, J.P., L.G. Van Uitert, W.H. Grodkiewicz and R.M. Mikulyak, 1986, J. Appl. Phys. 60, 4262.

- Van der Ziel, J.P., M.G. Oberg and R.A. Logan, 1987, Appl. Phys. Lett. **50**, 1313.
- Varsanyi, F., 1964, Excitation of fluorescence with monochromatic light in rare-earth crystals, in: Quantum Electronics, eds P. Brivet and N. Bloembergen (Dunod, Paris) p. 787.
- Vial, J.C., R. Buisson, F. Madeore and M. Poirier, 1979, J. Phys. 40, 913.
- Waite, T., 1964, J. Appl. Phys. 35, 1680.
- Wakabayashi, H., K. Mochizuki, Y. Namikura, S. Yamamoto, N. Edagawa and H. Taga, 1989, in: Proc. IOOC'89, Kobe, Japan, 18–21 July, 21, B2-4.
- Wang, Y., and J. Ohwaki, 1993, Appl. Phys. Lett. 63, 3268.
- Wannemacher, R., R.S. Meltzer and R.M. Macfarlane, 1990, J. Lumin. 45, 307.
- Weber, M.J., 1971, Phys. Rev. B 4, 2932.
- Weber, M.J., 1973, Phys. Rev. 138, 54.
- Weber, M.J., 1979, Rare earth lasers, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 4, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam) ch. 35.
- Weissbluth, M., 1989, Photon-Atom Interactions (Academic Press, London).
- Whitley, T.J., C.A. Millar, R. Wyatt, M.C. Brierley and D. Szebesta, 1991, Electron. Lett. 27, 1785.
- Yamada, N., S. Shionoya and T. Kushida, 1972, J. Phys. Soc. Jpn. 32, 1577.
- Yamamoto, Y., S. Machida, Y. Horikoshi, K. Igota and G. Björk, 1991, Opt. Commun. 80, 337.
- Yariv, A., 1967, Quantum Electronics (Wiley, New York).
- Yeh, D.C., W.A. Sibley, M.J. Suscavage and D.C. Drexhage, 1987, J. Appl. Phys. 62, 266.
- Yen, W.M., 1987, Experimental studies of energy transfer in rare-earth ions crystals, in: Spectroscopy of Solids Containing Rare-Earth Ions, eds A.A. Kaplyanski and R.M. Macfarlane (North-Holland, Amsterdam) p. 185.
- Yokota, M., and O. Tanimoto, 1967, J. Phys. Soc. Jpn. 22, 779.
- Zayhowski, J.J., and A. Mooradian, 1989, Opt. Lett. 14, 24.
- Zhou, B.W., and F. Auzel, 1993, Ann. Télécomm. (Paris) 48, 546.
- Zyskind, J.L., V. Mizrahi, D.J. Digiovanni and J.W. Sulkoff, 1992, Electron. Lett. 28, 1385.

Handbook on the Physics and Chemistry of Rare Earths Vol. 22 edited by K.A. Gschneidner, Jr. and L. Eyring © 1996 Elsevier Science B.V. All rights reserved

Chapter 152

ELECTRONIC STRUCTURE CALCULATIONS FOR MOLECULES CONTAINING LANTHANIDE ATOMS

Michael DOLG

Max-Planck-Institut für Physik komplexer Systeme, Dresden, Außenstelle Stuttgart, Heisenbergstr. 1, 70569 Stuttgart, Germany

Hermann STOLL

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Contents

	List	of sym	bols and abbreviations	608
1.	Intro	duction	1	609
	1.1.	Previo	us reviews and scope of the	
		presen	t review	609
	1.2.	Relativ	vistic and electron correlation	
		effects		614
	1.3.	The la	nthanide contraction	622
	1.4.	The su	perconfiguration model	627
2.	Met	nods		629
	2.1.	All-ele	ectron methods	630
		2.1.1.	Dirac-Coulomb-(Breit/Gaunt)	
			Hamiltonian	630
		2.1.2.	Douglas-Kroll-Hess Hamiltonian	636
		2.1.3.	Cowan-Griffin and Wood-Boring	
			schemes	638
		2.1.4.	Density-functional methods	640
	2.2.	Valenc	e-electron methods	641
		2.2.1.	Pseudopotentials, effective core	
			potentials and model potentials	642
		2.2.2.	Intermediate neglect of	
			differential overlap method	648
		2.2.3.	Extended Hückel method	650
		2.2.4.	Ligand field theory, angular	
			overlap model and other methods	650

7	D a sulta		651
5.	Results		001
	3.1. Atoms		651
	3.2. Diatomic	molecules	655
	3.2.1. Mo	onohydrides	655
	3.2.2. Mo	onoxides	660
	3.2.3. Mo	onofluorides	677
	3.2.4. Dir	mers	680
	3.2.5. Ra	re gas compounds	682
	3.2.6. Mi	scellaneous diatomics	682
	3.3. Polyatomi	ic molecules	684
	3.3.1. Hy	drides	684
	3.3.2. Ox	ides	684
	3.3.3. Ha	lides	685
	3.3.4. Sa	ndwich complexes	689
	3.3.5. Fu	llerene complexes	695
	3.3.6. Hy	drated lanthanide ions	700
	3.3.7. Mi	scellaneous polyatomics	703
	3.4. Solids		705
4.	Conclusions		715
	Acknowledger	nents	717
	Note added in	proof	718
	References		718

ACPF	averaged coupled-pair functional	INDO	intermediate neglect of differential
AE	all-electron		overlap
AIMP	ab initio model potential	k	force constant
AM1	Austin model 1	LFT	ligand field theory
с	velocity of light	MC	multi-configuration (self-consistent
CAS (CASSCF)	complete active space (self-consistent field)	(MCSCF) MNDO	field) modified neglect of differential
CC (CCSD)	coupled-cluster (with single and double substitutions)	MO-LCAO	overlap molecular orbitals by linear
CEPA	coupled electron pair approximation		combination of atomic orbitals
CG	CowanGriffin	MPn	Møller-Plesset perturbation theory to
CI (CISD)	configuration interaction (with single and double substitutions)	MR (MRCI)	nth order multi-reference (configuration
CIPSI	configuration interaction by	MC	interaction)
(CIPSO)	perturbative selection of the	MSLCAS	multiple scattering
	zeroth-order wavefunction (including spin-orbit interaction)	MS-LCAS	combination of atomic spinors
CNDO	complete neglect of differential	OCE	one-center expansion
	overlap	PP	pseudopotential
COSCI	complete open-shell configuration	QR	quasirelativistic
	interaction	R _e	bond length
D_{e}	binding energy	RCI	relativistic configuration interaction
D_0	dissociation energy	RHF	restricted Hartree-Fock
DFT	density-functional theory	SC	superconfiguration
DGCI	double group configuration	SCF	self-consistent field
	interaction	SOCI	second-order configuration
DHF	Dirac-Hartree-Fock	к.	interaction
DHFR	Dirac-Hartree-Fock-Roothaan	SW	scattered-wave
DHFS	Dirac-Hartree-Fock-Slater	UHF	unrestricted Hartree-Fock
DKH	Douglas–Kroll–Hess	WB	Wood–Boring
DV	discrete variational	α	fine structure constant
Ε	energy	α, β	Dirac matrices
ECP	effective core potential	$\mu_{ m e}$	dipole moment
EHT	extended Hückel	σ	Pauli matrices
FOCI	first-order configuration interaction	${\Phi}$	Slater determinant
$\Delta G_{1/2}$	energy difference between the $v=1$ and $v=2$ vibrational levels	φ	one-particle wavefunction (orbital, spinor)
${\cal H}$	Hamiltonian	ϕ_{e}	bond angle
HF	Hartree–Fock	Ψ	many-electron wavefunction
HFR	Hartree–Fock–Roothaan	ω_{e}	vibrational constant
HFS	Hartree–Fock–Slater		
Ι	identity matrix		

List of symbols and abbreviations

1. Introduction

1.1. Previous reviews and scope of the present review

In 1987 Pyykkö published a brief review of the available relativistic electronic structure calculations for f-element molecules. Of the 59 references summarized by Pyykkö only 10 are for lanthanides (57La-71Lu), whereas 53 are for actinides (89Ac-103Lr), most of them for Th and U. The applied methods range from ab initio all-electron Dirac-Hartree-Fock one-center-expansion or Dirac-Hartree-Fock-Slater calculations over quasirelativistic allelectron studies to semiempirical valence-only approaches like the intermediate neglect of differential overlap method or extended Hückel theory. Although all of these calculations include, to a certain extent, the major relativistic effects, none of them explicitly deals with electron correlation, which is now known to be equally important as relativity, especially for f-element systems. The references given by Pyykkö for the lanthanides are listed together with the available nonrelativistic calculations published in or prior to 1987 in table 1. It is noteworthy that the first papers reporting quantum-chemical calculations of lanthanide systems have been published as late as 1976. Surprisingly one of the most successful approaches of relativistic quantum chemistry (Kutzelnigg 1987), i.e. the pseudopotential, effective core potential or model potential method, has not been used for lanthanide compounds prior to 1989.

It might be asked why so little theoretical information is available for lanthanide compounds (fig. 1). The reasons are manifold. On the one hand theoretical chemists obviously were more interested in the heavier actinides since their variations in bonding properties, especially for uranium, are larger than for the lanthanides, and the relativistic effects are more pronounced (Pepper and Bursten 1991). On the other hand, as for the actinides, the electronic structure of lanthanide-containing systems is usually extremely complex, e.g. a $4f^7$ configuration gives rise to 119 LS states or 327 jj levels consisting of 3432 microstates (table 2). The numbers increase again dramatically when a singly occupied 5d orbital is present as in the ground states of some neutral lanthanide atoms (table 3).

If we consider for example the four-valence electron atoms ${}_{6}C$ (p block), ${}_{22}Ti$ (d block) and ${}_{58}Ce$ (f block) we experimentally find 1, 2 and 3 spatial configurations with a total of 3, 9 and 60 j levels, respectively, at term energies below 8000 cm⁻¹ (Moore 1949, 1952, 1958, Martin et al. 1978). Besides the large number of electronic states, many of which are low-lying in energy, the rather large relativistic and electron correlation effects have to be accounted for, which is quite costly and not at all a trivial task for first-principle investigations. The computational effort and the complexity of electronic structure ab initio calculations on molecules roughly increases with the largest angular quantum number of the occupied orbitals in the constituent atoms, i.e. d- and f-element systems pose a real challenge to quantum chemistry programs and computers. In a recent review in this handbook Jørgensen (1988) asked "Is Quantum Chemistry feasible?", and with special regard to the rare earths he answered "Sorry, not today; perhaps next century."

Method ^b	Molecules ^c	Reference
DHF-OCE	CeH ₄	Pyykkö and Desclaux (1978)
	YbH ⁺ , YbH ₂	Pyykkö (1979a)
	RH ($R = La, Tm, Lu$)	Pyykkö (1979b)
HF	LaX_3 (X=H, F, Cl)	Lohr and Jia (1986)
DHFS-DV	RX_3 (R = La, Ce, Nd, Gd, Er, Lu;X = F, Cl, Br, I)	Ruščić et al. (1983)
	$LaCl_3$, RX ₃ (R=La, Ce, Lu;X=Br, 1)	Ellis and Goodman (1984)
	TmS _n	Guo and Ellis (1984)
DHFS-MS	YbF ₆ ³⁻ , YbF ₈ ⁵⁻	Case and Lopez (1984)
QR-MS	Ce(cot) ₂	Rösch and Streitwieser (1983)
	Ce(cot) ₂	Rösch (1984)
	Ce(cot) ₂	Streitwieser et al. (1985)
X _a -DV	$Ce(OH_2)_{9}^{3+}$	Kobayashi et al. (1987)
X _a -MS	RF_3 (R = La, Ce, Yb)	Weber et al. (1977a)
	RF_3 (R = La, Ce, Pr, Nd), La Br_3 , La O_4^{5-}	Weber et al. (1977b)
INDO	$\operatorname{Ce}(\operatorname{cot})_{\overline{2}}$	Clack and Warren (1976)
	RF_3 , RF_8^{5-} (R = Ce, Nd, Sm, Gd, Tb, Tm, Yb)	Li et al. (1983), Ren et al. (1983)
	(pc)RCl	Li et al. (1986a)
	$(cp)_2LuClOC_4H_8$ and other compounds	Li et al. (1986b)
	$PrCl_3(OC_4H_5)_3$	Li et al. (1986c)
	$(Yb(cp)_2CH_3)_2$	Xu and Ren (1986)
	$\mathrm{Gd}_{10}\mathrm{C}_4\mathrm{Cl}_{18}$	Xu and Ren (1987)
	$[(CH_3C_5H_4)_2YbCl_2]_2$	Li et al. (1987a)
	(cp)NdClOC ₄ H ₈	Li et al. (1987b)
	RCl_2 (R = Sm, Eu, Yb), RCl_3 (R = La-Lu)	Culberson et al. (1987)
	RX_3 (R = Ce, Lu;X = F, Br, I), CeF ₄ , Ce(NO ₃) ₆ ²⁻	Culberson et al. (1987)
WHT	RX ₃	Bender and Davidson (1980)
QR-EHT	RI_3 (R = La-Lu)	Pyykkö and Lohr (1981)
	RX_3 (R = La, Nd, Gd, Lu;X = F, Cl, Br, I)	Lohr and Jia (1986)
EHT	RX_3 (R = La-Lu;X = F, Cl, Br, I)	Myers et al. (1978)
	$Sm(cp)_2^{q+}$ (q=0, 1), ((cp)_2SmH) _n (n=1, 2)	Ortiz and Hoffmann (1985)
	$R(cp)_2X$ (R=Sm, Lu; X=H, CH ₃)	Rabaâ et al. (1986)

 Table 1

 Electronic structure calculations on molecules containing lanthanide elements published up to 1987^a

^a Results are classified by method of calculation and, for each method, in chronological order. Ligand field and angular overlap calculations are not included. After Pyykkö (1987), with extensions.

^b Methods: DHF, Dirac-Hartree-Fock; DHFS, Dirac-Hartree-Fock-Slater; HF, Hartree-Fock; OCE, onecenter expansion; MS, multiple-scattering; DV, discrete-variational; QR, quasirelativistic; INDO, intermediate neglect of differential overlap; WHT, Wolfsberg-Helmholz; QR-EHT, quasirelativistic two-component extended Hückel; EHT, extended Hückel.

^c Abbreviations: cp, cyclopentadiene C₅H₅,

cot, cyclooctatetraene C₈H₈,

pc, phthalocyanine.



Fig. 1. Number of theoretical papers published in the period between 1978 and 1992 for atoms and molecules containing specified elements. The numbers have been obtained from the Quantum Chemistry Literature Data Base (Hosoya et al. 1993).

l	n	LS	jj	Μ	1	n	LS	ij	М
0	1	1	1	2	3	1, 13	1	2	14
1	1, 5	1	2	6		2,12	7	13	91
	2, 4	3	5	15		3, 11	17	41	364
	3	3	5	20		4,10	27	107	1001
2	1, 9	1	2	10		5, 9	73	198	2002
	2, 8	5	9	45		6, 8	119	295	3003
	3,7	8	19	120		7	119	327	3432
	4, 6	18	34	210					
	5	16	37	252					

Table 2 Number of LS terms (LS), jj terms (jj) and microstates (M) for an *l*ⁿ configuration^a

^a After Sobelman (1979), extended for jj terms.

Since the next century is not too far away, one may find some improvement of the situation analysed by Jørgensen, and indeed, in recent years much progress has been made to include relativistic effects and electron correlation effects in quantum-chemical electronic structure calculations for heavy-element systems like atoms and molecules of lanthanides and actinides. Two extensive bibliographies of the relativistic theory of atoms and molecules for the years 1916–1985 and 1986–1992 have been published by Pyykkö (1986, 1993). The fact that each of the two volumes contains more than 3000 references highlights the fast growth of the fields of relativistic atomic structure

La	$d^1 s^2 {}^2D_{3/2}$	Gd	$f^7 d^1 s^{2 9} D_2$	Ac	d ¹ s ² ² D _{3/2}	Cm	f ⁷ d ¹ s ² ⁹ D ₂
Ce	$f^1 d^1 s^2 {}^1G_4$	Tb	$f^9 s^2 {}^6H_{15/2}$	Th	$d^2 s^2 {}^3F_2$	Bk	f ⁹ s ² ⁶ H _{15/2}
Pr	$f^3 s^2 {}^4I_{9/2}$	Dy	f ¹⁰ s ^{2 5} I ₈	Pa	$f^2 d^1 s^2 {}^4K_{11/2}$	Cf	f ¹⁰ s ^{2 5} I ₈
Nd	$f^4 s^{2} {}^5I_4$	Но	$f^{11} s^2 {}^4I_{15/2}$	U	$f^3 d^1 s^{2} {}^5L_6$	Es	$f^{11} s^{24} I_{15/2}$
Pm	$f^5 s^2 {}^6H_{5/2}$	Er	$f^{12} s^{2} {}^{3}H_{6}$	Np	$f^5 s^2 {}^6H_{5/2}$	Fm	f ¹² s ^{2 3} H ₆
Sm	$f^6 s^2 {}^7F_0$	Tm	$f^{13} s^{2} {}^{2}F_{7/2}$	Pu	$f^6 s^2 {}^7F_0$	Md	$f^{13} s^{2} F_{7/2}$
Eu	$f^7 s^2 {}^8S_{7/2}$	Yb	$f^{14} s^{2} S_0$	Am	$f^7 s^2 {}^8S_{7/2}$	No	$f^{14} s^{2} S_0$
		Lu	$f^{14} \ d^1 \ s^{2 \ 2} D_{3\!/\!2}$			Lr	$f^{14} \ s^2 \ p^{1-2} P_{1/2}$

Table 3 Ground states for the lanthanide $({}_{s_7}La - {}_{71}Lu)$ and actinide $({}_{s_9}Ac - {}_{103}Lr)$ atoms^a

^a Data from Martin et al. (1978), Radzig and Smirnov (1985) and Blaise and Wyart (1992).

theory and relativistic quantum chemistry. Reviews specialized in relativistic atomic structure theory have been published by Grant (1970, 1983a-d, 1986, 1988), Lindgren and Rosén (1974) and Grant and Quiney (1988). Results of relativistic atomic Dirac-Hartree-Fock calculations for the ground-state configurational average of elements with nuclear charge Z = 1-120 have been published by Desclaux (1973). The corresponding nonrelativistic values are given for the nuclear charges Z = 1-100. Mann and Waber (1973) have published results of Dirac-Hartree-Fock calculations for the relativistic ground states of the neutral lanthanide atoms. Both tabulations also give the contributions of the magnetic and retardation terms in the electron interaction to the total energies. References for corresponding work of other authors have been listed by Pyykkö (1978, 1986, 1993). With the general availability of some of these modern atomic structure codes (Desclaux 1975, 1977, Grant et al. 1980, Dyall et al. 1989) and the increased computational resources at hand for many quantum chemists such tabulations have lost some of their importance: often the calculation for the atom in its specific electronic state in question can be run faster on a workstation than the information is recovered from the library. A number of review articles by various authors is available for relativistic electronic structure calculations on atoms and molecules, e.g. Pyykkö (1978, 1988a), Pitzer (1979), Pyykkö and Desclaux (1979a), Christiansen et al. (1985), Balasubramanian and Pitzer (1987), Ermler et al. (1988), Malli (1988) or Balasubramanian (1989). Some of these authors discuss the subject in general, others focus more or less on special topics like pseudopotential methods. Many contributions have also appeared in edited volumes, e.g. Wilson (1988a). Finally, several conference proceedings with articles related to relativistic quantum chemistry or quantum chemistry for d- and f-element systems are available, e.g. Malli (1983a, 1994a), Pyykkö (1984), Veillard (1986), Salahub and Zerner (1989) or Broer et al. (1994).

Admittedly the scope of the present review is rather limited. We will restrict ourselves to electronic structure calculations for molecules containing lanthanide atoms (La–Lu). Corresponding work on systems with actinide atoms (Ac–Lr) is only sometimes considered for the purpose of a comparison of 4f and 5f elements. An extensive review

on the electronic structure of actinide containing molecules has recently been published by Pepper and Bursten (1991) and the reader is referred to it for details. Atoms and especially solids are only briefly considered. The electronic structure methods discussed here are restricted to those that actually have been frequently applied to lanthanide systems, e.g. the pseudopotential method or the semiempirical intermediate neglect of differential overlap method, or to those which in the opinion of the authors will become important tools for future, possibly more accurate investigations, e.g. the relativistic Hartree–Fock self-consistent field and subsequent configuration interaction methods based on the Dirac–Coulomb–(Breit/Gaunt) or Douglas–Kroll–Hess Hamiltonian.

Today four-component Dirac-Hartree-Fock all-electron calculations for atoms are carried out almost routinely within finite difference schemes, and numerous publications have appeared. Large scale multiconfiguration self-consistent field studies including a large part of the electron correlation effects have recently become feasible (Cai et al. 1992). Less routine affairs are the corresponding investigations of atoms and small molecules within algebraic schemes, i.e. those using kinetically balanced finite basis sets. For these relativistic calculations the requirements in central processor time and disk space are considerably larger than for the nonrelativistic ones. Some of the existing computer programs have already been supplemented with subsequent correlation treatments like Møller-Plesset perturbation theory (Dyall 1994c), multireference configuration interaction (Esser 1983, 1984a,b, Visser 1992, Visser et al. 1992a,b, Visscher 1993, Visscher et al. 1993, 1994) or coupled-cluster methods (Eliav et al. 1994a,b, 1995). The one- or two-component Douglas-Kroll-Hess Hamiltonian (Hess 1986, Jansen and Hess 1989a) appears to yield rather accurate results and might be used alternatively to the more time-consuming Dirac-Hartree-Fock calculations. Both methods are especially useful for the calibration of more approximate computational ab initio schemes, e.g. for valence-only approaches like the pseudopotential, effective core potential or model potential methods. Relativistic parametrizations of these approximate ab initio schemes for the lanthanides (Dolg 1989, Dolg et al. 1989a,b, 1993a, Cundari and Stevens 1993, Ross et al. 1994) and actinides (Kahn et al. 1978, Ermler et al. 1991, Küchle 1993, Küchle et al. 1994) have also become available recently. Corresponding electronic structure codes that also allow for an inclusion of spin-orbit effects besides the scalar relativistic effects together with a fairly accurate treatment of electron correlation have also been developed during the last years (Teichteil et al. 1977, Christiansen et al. 1982, Esser 1983, 1984a,b, A.H.H. Chang and Pitzer 1989, Balasubramanian 1989). Densityfunctional approaches have become increasingly popular in quantum chemistry. Some attempts to derive relativistic extensions exist (Ramana and Rajagopal 1983), however their application to lanthanide systems seems to face problems due to the compact and often only partially occupied 4f shell (Wang et al. 1995). On the side of the semiempirical methods, in addition to the frequently used relativistically parametrized two-component extended Hückel method (Lohr and Pyykkö 1979, Pyykkö 1988b) the intermediate neglect of differential overlap approach adapted for ground-state properties (Ren et al. 1982, Li et al. 1983, Culberson et al. 1987) and for spectroscopy (Kotzian 1991, Kotzian et al. 1992) has been extended quite successfully to the lanthanides. Recent attempts to obtain the corresponding parametrizations for the actinides seem to yield less satisfactory results, probably due to missing reference data (Cory et al. 1994). Ligand field theory has been frequently applied to explain experimentally observed spectra for lanthanide diatomics (Field 1982). An alternative treatment is the angular overlap model (Urland 1976). Both approaches are certainly useful to interpret experimental data but have a rather limited predictive power and will not be treated in detail here. The same is true for schemes like the multipole expansion method or polarized ion model (Rittner 1951).

Further, the emphasis of our review is on calculations that include both relativistic and electron correlation effects. Nonrelativistic calculations are usually only mentioned when a corresponding relativistic calculation is available and allows us to determine relativistic effects. Uncorrelated calculations will not be discussed whenever corresponding results including correlation effects are available. There exists far more experimental than theoretical information on lanthanide systems, and only a few of the important experimental papers can be cited in this article. We refer to the theoretical papers reviewed here for a more complete list of citations.

Finally, a review of relativistic effects and the electronic structure of lanthanide and actinide molecules has recently been published by Balasubramanian (1994) in this Handbook Series (Vol. 18, ch. 119). Topics treated in more detail by Balasubramanian, e.g. the effects of the lanthanide contraction on the 5d transition metals, have been kept rather brief in the present article. Although it is not possible to completely avoid overlap with the review by Balasubramanian, we hope that the reader still benefits from the present contribution.

1.2. Relativistic and electron correlation effects

Accurate quantum-chemical calculations on heavy-element compounds have to take into account both relativistic and electron correlation effects. Although an exact relativistic many-electron Hamiltonian is not known up to now whereas electron correlation can be treated to any desired accuracy in principle, it turns out in practical applications for d and f element systems that relativistic effects can be treated with higher accuracy than electron correlation effects. Therefore, relativistic terms in the Hamiltonian may be included only in an approximate way leading to less computationally demanding schemes without significant loss of the overall accuracy of the calculation. From the comparison of Dirac-Hartree-Fock all-electron studies based on the Dirac-Coulomb and Dirac-Coulomb-(Breit/Gaunt) Hamiltonian it became obvious that for most chemical problems it is sufficient only to consider the relativistic one-particle effects due to the Dirac Hamiltonian in the calculations, cf. e.g. the early Dirac-Hartree-Fock one-center expansion studies on PbH₄ by Pyykkö (1978) or corresponding more recent results obtained with the Dirac-Hartree-Fock-Roothaan scheme by Visser et al. (1992a). Instead of a fully relativistic four-component treatment based on the Dirac equation it is desirable to derive simpler two-component quasirelativistic formulations, e.g. in the quasirelativistic Pauli equation the Dirac Hamiltonian corresponds to the mass-velocity, Darwin and spinorbit terms which have to be added to the nonrelativistic Schrödinger Hamiltonian.

The hydrogen-like solutions of the Dirac equation are always found at lower energy than the corresponding solutions of the nonrelativistic Schrödinger equation. The stabilization results from the mass-velocity term of the Pauli equation, whereas the Darwin term leads to a weaker destabilization. The absolute value of the stabilization decreases with increasing main quantum number n and for a given n with increasing angular quantum number l. Along with the stabilization goes a contraction of the radial density. Finally, the spin-orbit term splits the one-electron states with $l \ge 1$ into two components of total angular momentum quantum number $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$. After the inclusion of spinorbit interaction one also has to consider the changed symmetry properties of the oneparticle solutions which are now called spinors and transform according to irreducible representations of the double group in contrast to the orbitals which transform according to irreducible representations of the usual single group. The changes that result from the application of the Dirac (or Pauli) Hamiltonian instead of the Schrödinger Hamiltonian for one-particle states are called direct relativistic effects. Whereas the nonrelativistic energy of a one-electron atom with nuclear charge Z increases as Z^2 , the lowest-order relativistic corrections are proportional to Z^4 .

In a many-electron atom the direct relativistic effects act on all orbitals. However, not always are stabilization and contraction observed. At first glance the following simple picture is obvious. The s and inner p orbitals undergo a strong stabilization (as judged from orbital energies) and contraction (as judged from $\langle r \rangle$ expectation values). For the valence p orbitals of most atoms the stabilization is small, however the contraction is still present. Therefore, the nuclear charge for the d and f orbitals is shielded more effectively by the inner s and p shells and, since for them the direct relativistic effects are relatively weak, they undergo a net destabilization and expansion. The destabilization and expansion due to a more efficient screening of the nuclear charge by contracted inner shells is called an indirect relativistic effect or relativistic self-consistent field effect. It should be noted that both direct and indirect effects act on all orbitals of a many-electron atom. Usually the direct effects are dominating for s and p shells, resulting in a stabilization and contraction, whereas for d and f shells the indirect effects are larger, leading to destabilization and expansion. The direct relativistic effects originate in the immediate vicinity of the nucleus, whereas in particular the outer core shells contribute to the indirect effects (Schwarz et al. 1989).

When spin-orbit interaction is included things become more complicated. An overview for nuclear charges from 1 to 100 may be obtained from the plots published by Desclaux (1973). The actual numbers for Ce and Lu are given in table 4. It is noteworthy that the spin-orbit splitting of the 4f shell increases strongly from 0.28 eV (Ce) to 1.76 eV (Lu), whereas the one for the 5d shell increases slightly from 0.14 eV (Ce) to 0.17 eV (Lu). The $s_{1/2}$ and $p_{1/2}$ shells are always stabilized and contracted, the relative magnitude of the effects increasing strongly with the nuclear charge. The $p_{3/2}$ and $d_{3/2}$ valence shells are destabilized and contracted with increasing nuclear charge. The $d_{5/2}$, $f_{5/2}$ and $f_{7/2}$ shells are always destabilized and expanded, the relative magnitude of the effects decreasing with increasing nuclear charge. Some of the data for the lanthanide series are shown

respectively. The ratio of relativistic and corresponding nonrelativistic values is given in parentheses. Data taken from Desclaux (1973)							
AS	Ce	2	Lu	l			
	ϵ	$\langle r \rangle$	έ	$\langle r \rangle$			
4f _{5/2}	-0.5414	1.0365	-0.8553	0.6942			
4f _{7/2}	-0.5310 (0.7599)	(1.0340) 1.0444 (1.0620)	(0.7943) -0.7908 (0.7344)	0.7081 (1.0496)			
5s _{1/2}	-1.8857 (1.0751)	1.5349 (0.9578)	-2.7017 (1.1660)	1.1924 (0.9184)			
5p _{1/2}	-1.1606 (1.0768)	1.7162 (0.9563)	-1.6258 (1.1817)	1.3337 (0.9119)			
5p _{3/2}	-1.0515 (0.9755)	1.7938 (0.9995)	-1.3579 (0.9870)	1.4436 (0.9870)			
5d _{3/2}	-0.2389 (0.8834)	2.8174 (1.0383)	-0.1913 (0.7863)	2.6944 (1.0841)			
5d _{5/2}	-0.2339 (0.8649)	2.8654 (1.0560)	-0.1850 (0.7603)	2.7792 (1.1182)			
6s _{1/2}	-0.1826 (1.0576)	4.6487 (0.9548)	-0.2225 (1.1189)	3.9024 (0.9163)			

Table 4

Orbital energies ϵ (a.u.) and radial expectation values $\langle r \rangle$ (a.u.) for the valence shells of Ce and Lu from multiconfiguration Dirac–Hartree–Fock calculations for the average of the 4f¹ 5d¹ 6s² and 4f¹⁴ 5d¹ 6s² configurations, respectively. The ratio of relativistic and corresponding nonrelativistic values is given in parentheses. Data taken from Desclaux (1973)



Fig. 2. Ratio of relativistic and nonrelativistic orbital energies for the valence orbitals of the lanthanide atoms in their ground state configuration. Data taken from Desclaux (1973).

in figs. 2 and 3. For the valence orbitals of the lanthanides we note that no monotonic behavior is found along the series due to the variations in the ground state configuration. The $4f_{5/2}$ and $4f_{7/2}$ shells are strongly destabilized by 20–35% but only slightly expanded



Fig. 3. Ratio of relativistic and nonrelativistic $\langle r \rangle$ expectation values for the valence orbitals of the lanthanide atoms in their ground state configuration. Data taken from Desclaux (1973).

by 3–8%. The $5d_{3/2}$ and $5d_{5/2}$ shells of La, Ce, Gd and Lu are destabilized by 11-24%and expand by 4–12%. The $6s_{1/2}$ shell is stabilized by 5–12% and contracts by 4–8%. We want to note here that relativistic contractions or expansions of valence orbitals are not due to orthogonality constraints with respect to inner contracted or expanded orbitals as has often been stated in older articles (Pyykkö and Desclaux 1979a, Balasubramanian and Pitzer 1987). This is quite obvious from quasirelativistic atomic structure calculations within the Cowan-Griffin (Cowan and Griffin 1976) or Wood-Boring (Wood and Boring 1978) scheme, where valence orbital contractions or expansions are accurately described without imposing orthogonality requirements for the orbitals. For further information on the spatial origin of relativistic effects in atoms and the resulting conclusions for valence-only methods we refer to the original articles (Schwarz et al. 1989, Schwarz 1990, Baerends et al. 1990). It should also be noted that a direct comparison of orbital $\langle r \rangle$ expectation values from Dirac-Hartree-Fock and Hartree-Fock calculations is actually not allowed since one is working within different pictures (Snijders and Pyykkö 1980, Baerends et al. 1990); however, for the valence orbitals considered here the inaccuracies inherent to such an approach are certainly smaller than the relativistic effects themselves.

Before concluding the discussion of relativistic effects in atoms we want to add that, as always, exceptions might exist. A contraction of s and p shells due to direct relativistic effects leads to the indirect destabilization of d and f shells, but this indirect destabilization of the d and f shells may in turn have a stabilizing effect on outer s and p shells due to the nuclear charge being less efficiently screened, i.e., it causes an indirect stabilization. It is accepted that the 6s shell of Au and Hg is stabilization of 6s due to the diffuse 4f and 5d shells was found to overcompensate the indirect destabilization mainly due to the contracted 5s and 5p shells for Hg (Desclaux 1972) or just to compensate it for Au (Rose et al. 1978). An analysis has been given by Schwarz et al. (1989).

Besides the effects of relativity those of electron correlation are very important for d and f elements. Unfortunately, except for simple systems, correlation cannot be treated as accurately as relativity. Moreover, for a discussion it is necessary to look at quantum-mechanical observables like ionization and excitation energies instead of one-particle properties like orbital energies and radial expectation values. Therefore, in order to discuss correlation effects in atoms we assume that correlation contributions may be derived as the difference between experimental data and theoretical results obtained from an uncorrelated relativistic calculation, e.g. a relativistic Dirac-Hartree-Fock or a quasirelativistic Wood-Boring calculation. For comparison the corresponding relativistic contributions are calculated as the difference between theoretical values from an uncorrelated relativistic and a corresponding nonrelativistic calculation, e.g. a Hartree-Fock calculation. We note that the assumed additivity of contributions from electron correlation and relativity is only valid as a first approximation. Especially for heavier elements the relativistic operators change the total electron density distribution significantly, which in turn leads to different correlation energies as is obvious from basic density-functional theory.

For the excitation and ionization energies of the d transition metals a systematic study has been performed by Martin and Hay (1981). They compared experimental data with theoretical results derived from quasirelativistic Cowan-Griffin and nonrelativistic Hartree-Fock calculations. Similar results for relativistic contributions to excitation and ionization energies are available for the lanthanides (Dolg et al. 1989a) and actinides (Küchle et al. 1994). The data given there for the correlation contributions, however, have to be viewed with some care, since it is not always possible to properly average over the Jlevels of a given LS-term. As a rule of thumb it is found that electron correlation stabilizes configurations with higher d and f occupation numbers, whereas relativity stabilizes configurations with higher s and p occupation numbers and destabilizes those with higher d and f occupation numbers. As an example one might look at the $4f^n 5d^1 6s^2 \rightarrow 4f^{n+1} 6s^2$ excitation energies for the lanthanides La (n=0) through Yb (n=13) displayed in fig. 4. It can be seen that relativity stabilizes the configurations with the lower f occupation number, whereas electron correlation acts in the opposite direction. Relativistic contributions range from approximately 3 eV for La to 5 eV for Yb, whereas correlation contributions are -1 eV for La and -3 eV for Yb.

With special regard to the lanthanide and actinide elements we find that the increasing destabilization of the f shell in the latter causes a preference of low-lying states with occupied d orbitals, e.g. the Ce ground state is $4f^{1}5d^{1}6s^{2} {}^{1}G_{4}$, whereas that of Th is $6d^{2}7s^{2} {}^{3}F_{2}$. It is often stated in the literature that the actinide 5f orbitals are relativistically strongly destabilized and therefore more accessible for chemical bonding than the more or less core-like 4f orbitals of the lanthanides. This phenomenon is not exclusively a consequence of relativity, but is also due to the fact that the 4f orbitals have no orthogonality constraints with respect to inner orbitals of the lowest shell of a given symmetry is also observed for 2p and 3d in comparison to 3p and 4d, respectively. Such missing orthogonality requirements have been coined missing 'primogenic repulsion' (Pyykkö 1979b).



Fig. 4. $4f^{n}5d^{1}6s^{2} \rightarrow 4f^{n+1}6s^{2}$ excitation energies (eV) of La through Yb from nonrelativistic Hartree–Fock (nrel.) and quasirelativistic Wood–Boring (rel.) calculations (Dolg et al. 1989b) in comparison to experimental data (exp.) (Martin et al. 1978).

It is more difficult to discuss relativistic and correlation effects for molecules than for atoms. Most of the atoms have low-lying electron configurations with s and p orbitals being those with the largest radial extent, e.g. $ns^i np^j$ for main group elements, $(n-1)d^k ns^i$ for transition elements and $(n-2)f^l ns^i$ or $(n-2)f^l (n-1)d^k ns^i$ for lanthanides and actinides. Since the s and p shells usually contract it is no surprise that most molecules show a relativistic bond length contraction. However, when the (n-1)d and (n-2)f orbitals are involved in chemical bonding, relativistic bond length expansions might be expected as it is indeed the case for some lanthanide and actinide compounds, e.g. 0.05 Å for CeO (Dolg et al. 1991a) and 0.13 Å for ThO (Küchle et al. 1994). We note here in passing that the ground state configuration of CeO corresponds to $\phi_{Ce4f}^1 \sigma_{O2p}^2$ $\pi_{O2p}^4 \sigma_{Ce6s,6p}^1$ whereas that of ThO is rather $\sigma_{Th7s}^2 \sigma_{O2p}^2 \pi_{O2p}^4$, i.e. the relativistic effects in the atoms are also present in the molecules. In addition to the relativistic changes of bond lengths one also finds relativistic effects for bond angles, e.g. CeO_2 is found to be bent (O-Ce-O bond angle 132°) and linear in quasirelativistic and nonrelativistic densityfunctional calculations, respectively (Heinemann et al. 1996). A collection of data for relativistic bond length changes for the whole periodic system may be found in the review by Pyykkö (1988a), and a corresponding shorter compilation for the lanthanides is listed in table 5.

Since bond length contractions and orbital contractions often are comparable in magnitude and direction it was assumed without further proof that the first were caused by the latter, cf. e.g. Pyykkö and Desclaux (1979a). However, in 1980 the so-called 'Dutch Revolution' (Pyykkö 1988a) took place and it was shown (Snijders and Pyykkö 1980, Ziegler et al. 1980, 1981, Pyykkö et al. 1981) that both effects are indeed often

Method ^a	Molecule	$R_e^r - R_e^{nr}$	$D_e^r - D_e^{nr}$	Reference
DHF/HF-OCE	LaH $4f^{0}\sigma^{2}\sigma^{1}$	0.012	-0.13	Pyykkö 1979b
	LuH 4f ¹⁴ $\sigma^2\sigma^1$	-0.006	0.41	
QR-DFT⁵	LaH $4f^0\sigma^2\sigma^1$	-0.03	-0.12	Wang and Schwarz 1995
	GdH $4f^{7}\sigma^{2}\sigma^{1}$	-0.02	-0.14	
	LuH $4f^{14}\sigma^2\sigma^1$	-0.03	-0.03	
	LaO $4f^0\sigma^2\pi^4\sigma^1$	0.00	-1.22	
	GdO $4f^7\sigma^2\pi^4\sigma^1$	-0.04	-2.92	
	LuO $4f^{14}\sigma^2\pi^4\sigma^1$	0.00	-0.85	
	LaF $4f^0\sigma^2\pi^4\sigma^2$	-0.03	-1.24	
	GdF 4f ⁷ $\sigma^2 \pi^4 \sigma^2$	-0.07	-1.36	
	LuF $4f^{14}\sigma^2\pi^4\sigma^2$	-0.01	0.09	
	CeO_2	0.043 ^b		Heinemann et al. 1996
	CeO_2^+	0.044 ^b		
P₽ [₿] , CI	LaH $4f^0\sigma^2\sigma^1$	0.014	0.15	Dolg and Stoll 1989
	LuH $4f^{14}\sigma^2\sigma^1$	0.015	0.45	
	CeO $4f^1\sigma^2\pi^4\sigma^1$	0.041	-0.80	Dolg et al. 1991a
	EuO 4f ⁷ $\sigma^2 \pi^4$	0.005	-0.77	Dolg et al. 1990b
	EuO 4f ⁶ $\sigma^2 \pi^4 \sigma^1$	0.025	2.57	
	GdO $4f^{7}\sigma^{2}\pi^{4}\sigma^{1}$	0.016	-0.25	Dolg et al. 1990a
	YbO $4f^{14}\sigma^2\pi^4$	0.008	-0.84	Dolg et al. 1992c
	YbO $4f^{13}\sigma^2\pi^4\sigma^1$	0.016	3.80	

Table 5 Relativistic bond length (Å) and energy (eV) changes for selected lanthanide molecules

^a Methods: CI, configuration interaction; DFT, density-functional theory; DHF, Dirac-Hartree-Fock; HF, Hartree-Fock; OCE, one-center expansion; PP, pseudopotential; QR, quasirelativistic.

^b The PP results and the QR-DFT results of Heinemann et al. (1996) do not include spin-orbit interaction. Heinemann et al. (1996) found CeO_2 to be linear (bent) in nonrelativistic (relativistic) calculations, whereas CeO_2^+ is always linear.

parallel, but largely independent. It was possible to reproduce relativistic bond-length contractions by using nonrelativistic orbitals together with a relativistic Hamiltonian in first-order perturbation theory, i.e. the bond-length contraction is not caused by orbital contractions. The main reason for a bond-length contraction appeared to be the direct relativistic stabilization acting on the tails of the valence orbitals extending to the nuclei. Finally, Schwarz et al. (1983) and Schwarz (1987, 1990) provided the missing clarification and showed that both interpretations are valid, but have to be supplemented by a third one to be used for pseudopotential calculated as a quantum-mechanical observable, the two interpretations start from the integrands of the corresponding expectation values. Although the values of the integrals are identical, the integrands may differ and therefore allow different interpretations. The total energy E of a diatomic molecule in a given

electronic state is a function of the internuclear distance R and the velocity of light, e.g. of c^{-2} . From the total differential of E,

$$dE = \frac{\partial E}{\partial R} dR + \frac{\partial E}{\partial c^{-2}} d(c^{-2}), \qquad (1)$$

one may derive the relativistic bond-length change,

$$\Delta R_{\rm e} = c^{-2} \left. \frac{\mathrm{d}R}{\mathrm{d}(c^{-2})} \right|_{\mathrm{d}E/\mathrm{d}R=0} = k^{-1} \frac{\partial^2 E}{\partial R \,\partial r},\tag{2}$$

where $k = \partial^2 E/\partial R^2$ denotes the harmonic force constant and $r = \ln c^2$. Inserting the expectation value for the total energy $E = \langle \Psi | \mathcal{H} | \Psi \rangle$ of a normalized wavefunction leads to the following two equivalent interpretations valid for all-electron calculations based on the Dirac-Coulomb Hamiltonian, for which $(\partial^2 \mathcal{H}/\partial R \partial r) = 0$ holds.

Interpretation 1 (traditional explanation): the change of the Hellmann–Feynman force $\langle \partial \mathcal{H} / \partial R \rangle$ due to relativistic changes of the wavefunction $\partial \Psi / \partial r$, i.e. orbital expansions and contractions, causes relativistic bond length changes:

$$\Delta R_{\rm e} = k^{-1} \frac{\partial \langle \Psi | \partial \mathcal{H} / \partial R | \Psi \rangle}{\partial r} = k^{-1} \langle \Psi | \partial \mathcal{H} / \partial R | \partial \Psi / \partial r \rangle + {\rm c.c.}$$
(3)

Interpretation 2 (Dutch explanation): the change of the contributions of relativistic, i.e. c-dependent, terms in the Hamiltonian $\langle \partial \mathcal{H} / \partial r \rangle$ due to changes in the wavefunction upon molecular formation $\partial \Psi / \partial R$, causes relativistic bond length changes:

$$\Delta R_{\rm e} = k^{-1} \frac{\partial \langle \Psi | \partial \mathcal{H} / \partial r | \Psi \rangle}{\partial R} = k^{-1} \langle \Psi | \partial \mathcal{H} / \partial r | \partial \Psi / \partial R \rangle + {\rm c.c.}$$
(4)

In pseudopotential calculations one has a different nodal structure of the pseudovalence orbitals in comparison to the all-electron valence orbitals. $(\partial^2 \mathcal{H}/\partial R \partial r)$ and its expectation values are neither vanishing nor small. On the contrary, it is assumed and has numerically been shown for Au₂ that the main contribution to the relativistic bond-length changes stem from relativistic corrections to the Hellmann–Feynman force resulting from the pseudopotential:

$$\Delta R_{\rm e} \approx k^{-1} \left\langle \Psi \left| \partial^2 \mathcal{V} / \partial R \, \partial r \right| \Psi \right\rangle. \tag{5}$$

The relativistic changes to be expected in bond energies according to Schwarz (1990) and Pyykkö (1988a) are summarized in table 6. We note that the term 'decisive orbital' used in this table refers to an atomic valence orbital that is significantly involved in the formation of the chemical bond. In view of the core-like character of the 4f shell in most of the lanthanide compounds the 4f orbitals are not to be considered as decisive orbitals in this context. These are rather the 5d and 6s valence orbitals. Spin–orbit effects also play an important role here, since spin–orbit coupling always stabilizes the ground states of

621

Dominant relativistic	Decisive	Covalent	Ionic bonding		
effect	AO	bonding	Heavy cation	Heavy anion	
Direct stabilization	s _{1/2}	increase	decrease	increase	
Spin-orbit stabilization	p _{1/2} , d _{3/2}	decrease	decrease	increase	
Spin-orbit destabilization	p _{3/2} , d _{5/2}	decrease	increase	decrease	
Indirect destabilization	d, f	increase	increase	decrease	

Table 6 Relativistic bond energy changes^a

^a Reproduced from Schwarz (1990).

the separated atoms, but it is often quenched in the molecule. In general, bonding orbitals are destabilized, whereas antibonding orbitals are stabilized (Hafner et al. 1981), however hybridization and configuration interaction may limit the usefulness of this simple picture. Again this rule of thumb may hold for valence orbitals, but usually not for the core-like open 4f shells of the lanthanides. For an instructive overview on the fundamentals of relativistic effects in chemistry we refer to the article written by Schwarz (1990).

There are also correlation contributions to molecular properties, e.g. bond energies usually are increased. The correlation effects on bond lengths and angles and vibrational frequencies are probably not easy to predict for d and f element compounds. Although the 4f shell usually does not play a direct role in covalent chemical bonding, it contributes in some cases significantly to energetics, e.g. binding energies. This is always the case when formally the 4f occupation number in the ground state of the molecule and the lanthanide atom are not identical. For example, for the monoxide of $_{59}$ Pr it is known that one has approximately 4f occupation numbers of 3 in the atom (Pr $4f^36s^2$) and 2 in the molecule ($Pr^{2+} 4f^26s^1 O^{2-}$), respectively. The corresponding rearrangement of the 4f shell upon formation of a chemical bond influences ionic bonding and also brings about large differential relativistic and correlation effects.

Solids are also influenced by relativistic (Koelling and MacDonald 1983) and electron correlation (Fulde 1991) effects. For a discussion we have to refer to the literature summarized, e.g., by Pyykkö (1986, 1993).

1.3. The lanthanide contraction

Across the lanthanide series, ${}_{57}La$ (4f⁰5d¹6s² ${}^{2}D_{3/2}$) to ${}_{71}Lu$ (4f¹⁴5d¹6s² ${}^{2}D_{3/2}$), the 4f shell is filled. Although the 4f orbitals are rather compact in shape (fig. 5) they do not completely shield the corresponding increase of the nuclear charge for the more diffuse 5d, 6s and 6p valence orbitals. As a consequence a contraction of the radial expectation values $\langle r \rangle$ or radii of maximum charge density r_{max} of the valence orbitals is observed in atomic calculations. A similar effect occurs when the 5f shell is filled across the actinide series, ${}_{89}Ac$ (5f⁰6d¹7s² ${}^{2}D_{3/2}$) to ${}_{103}Lr$ (5f¹⁴7s²7p¹ ${}^{2}P_{1/2}$). We note here in passing that for Lr the 5f¹⁴7s²6d¹ ${}^{2}D_{3/2}$ state is calculated 5270 cm⁻¹ above the 5f¹⁴7s²7p¹ ${}^{2}P_{1/2}$ state in single-configuration all-electron Dirac–Hartree–Fock calculations including the



Fig. 5. Radial parts of the Dirac–Hartree–Fock valence spinors of Ce in the 4f¹5d¹6s² ground state configuration. Calculated with the program GRASP (Dyall et al. 1989).

Breit interaction and corrections from quantum electrodynamics (Küchle 1993). On the basis of corresponding more extensive multi-configuration calculations together with an estimated correction for neglected correlation effects Desclaux and Fricke (1980) derived a ${}^{2}D_{3/2}$ term energy of $(1.5\pm1)\times10^{3}$ cm⁻¹. Recent more extensive calculations (Wijesundera et al. 1995) yielded a value of 1679 cm⁻¹, however the authors do not reach a definite conclusion due to the limitations in the correlation treatments of their and previous work. In order to obtain reliable information about the effect of filling the f shell one should of course use corresponding states for the atoms at the beginning and end of the row. Therefore, within a one-particle model one may derive theoretical values for the lanthanide and the corresponding actinide contraction according to

$$\Delta_{\text{Lanthanide}} = \langle r \rangle (nl, \text{La}^{q+}) - \langle r \rangle (nl, \text{Lu}^{q+}),$$

$$\Delta_{\text{Actinide}} = \langle r \rangle (nl, \text{Ac}^{q+}) - \langle r \rangle (nl, \text{Lr}^{q+}),$$
(6)

where $\langle r \rangle$ also might be replaced by r_{max} . In Dirac–Slater calculations Waber and Cromer (1965) found a decrease in r_{max} for 5p of 0.190 Å for La to Lu and of 0.189 Å for La³⁺ to Lu³⁺, respectively. Similar values for r_{max} and $\langle r \rangle$ of 5p_{3/2} in La to Lu can be derived from the tabulation of Dirac–Hartree–Fock results of Desclaux (1973), i.e., 0.198 Å and 0.207 Å, respectively. Table 7 summarizes some atomic results for the lanthanide contraction together with those for the actinide contraction. It is obvious from the listed data that the actual value largely depends on the valence orbital and its spin–orbit component one is looking at. Moreover, the effects are larger for the first half of each series than for the second half. This is due to the fact that the 4f and

Method ^b		Lanthanides			Actinides			
	Atoms	Orbital	Value ^c (Å)	Atoms	Orbital	Value ^c (Å)		
DHF	La–Lu (Gd)	5p _{1/2}	0.225 (0.131)	Ac–Lr (Cm)	6p _{1/2}	0.270 (0.162)		
	La–Lu (Gd)	5p _{3/2}	0.207 (0.122)	Ac–Lr (Cm)	6p _{3/2}	0.240 (0.152)		
	La–Lu (Gd)	5d _{3/2}	0.090 (0.100)	Ac–Lr (Cm)	6d _{3/2}	0.183 (0.213)		
	La–Lu (Gd)	5d _{5/2}	0.070 (0.091)	Ac–Lr (Cm)	6d _{5/2}	0.144 (0.196)		
	La–Lu (Gd)	6s _{1/2}	0.434 (0.236)	Ac–Lr (Cm)	$7s_{1/2}$	0.490 (0.275)		
HF	La–Lu (Gd)	5p	0.196 (0.116)	Ac–Lr (Cm)	6р	0.213 (0.132)		
	La–Lu (Gd)	5d	0.144 (0.109)	Ac–Lr (Cm)	6d	0.254 (0.180)		
	La–Lu (Gd)	6s	0.356 (0.200)	Ac–Lr (Cm)	7s	0.335 (0.197)		
DHF	La ³⁺ –Lu ³⁺ La ³⁺ –Lu ³⁺	5p _{1/2} 5p _{3/2}	0.215 0.198	Ac ³⁺ –Lr ³⁺ Ac ³⁺ –Lr ³⁺	6p _{1/2} 6p _{3/2}	0.259 0.228		
HF exp.	La ³⁺ –Lu ³⁺ La ³⁺ –Lu ³⁺	5p	0.188 0.171	$Ac^{3+}-Lr^{3+}$ $Ac^{3+}-Lr^{3+}$	6р	0.204 0.184		

Table 7 Values for the lanthanide and actinide contraction from various atomic calculations^a

^a Calculated with the program GRASP (Dyall et al. 1989).

^b Methods: HF, Hartree–Fock; DHF, Dirac–Hartree–Fock; exp., values from experimentally derived ionic radii for the M³⁺ ions and coordination number 6 (Shannon 1976, David et al. 1978).

^c Values in parentheses correspond to the contraction for the first half of the series.

5f orbitals become more core-like along the lanthanide and actinide series and therefore shield the increasing nuclear charge more efficiently. As a result the lanthanide and actinide contractions for the 5d and 6d shells even show a maximum near Gd and Cm, respectively. Relativistic contributions to the lanthanide and actinide contractions are also dependent on the orbital under consideration, e.g. 14.8% ($5p_{1/2}$), 5.6% ($5p_{3/2}$), -37.5% ($5d_{3/2}$), -51.4% ($5d_{5/2}$) and 21.9% ($6d_{51/2}$) for La–Lu, and 26.8% ($6p_{1/2}$), 12.7% ($6p_{3/2}$), -28.0% ($6d_{3/2}$), -43.3% ($6d_{5/2}$) and 46.3% ($7s_{1/2}$) for Ac–Lr.

Of course, the orbital related values extracted from atomic structure calculations are no expectation values of quantum-mechanical observables. Moreover, effects of electron correlation are not included in these theoretical values. Therefore, one might look at ionic and atomic radii derived from the lattice constants of solids (Shannon and Prewitt 1969, Shannon 1976, David et al. 1978) or observables like bond lengths of molecules, e.g.

$$\Delta_{\text{Lanthanide}} = R_{\text{e}}(\text{LaX}) - R_{\text{e}}(\text{LuX}), \qquad \Delta_{\text{Actinide}} = R_{\text{e}}(\text{AcX}) - R_{\text{e}}(\text{LrX}). \tag{7}$$

	(nomenaryshe) me	localar calculations an	a experimentar data		
Method ^a	Lant	thanides	Actinides		
	Molecules	Value (Å)	Molecules	Value (Å)	
DHF(HF)-OCE	LaH–LuH ^b	0.209 (0.191)	AcH–LrH ^b	0.330	
QR-DFT	LaH–LuH ^g	0.19 (0.19)			
PP, CI	LaH–LuH ^d	0.106 (0.107)	AcH–LrH ^e	0.184 (0.130)	
DHF(HF)-OCE	CeH ₄ –HfH ₄ °	0.190 (0.164)	ThH4-(104)H4 h	0.30	
QR-DFT	LaO–LuO ^g	0.06 (0.06)			
PP, CI	LaOLuO ^d	0.022 (0.006)	AcO–LrO ^c	0.057 (0.005)	
exp.		0.036			
QR-DFT	LaF–LuF ^g	0.12 (0.14)			
PP, CI	LaF–LuF ^d	0.094 (0.071)	AcFLrF°	0.150 (0.091)	
exp.		0.11			
PP, CI	LaF ₃ -LuF ₃ ^f	0.198	AcF ₃ -LrF ₃ ^e	0.212 (0.125)	
exp.		0.20			

Table 8 Values for the lanthanide and actinide contraction derived from bond lengths from various relativistic (nonrelativistic) molecular calculations and experimental data

^a Methods: CI, configuration interaction; DFT, density-functional theory; DHF, Dirac-Hartree-Fock; HF, Hartree-Fock; OCE, one-center expansion; PP, pseudopotential; QR, quasirelativistic.

^b Pyykkö (1979b).

° Pyykkö and Desclaux (1978).

^d Quasirelativistic 11 valence electron pseudopotentials for La and Lu. Basis sets: La, Lu (8s7p6d6f), H (8s4p3d2f), O, F (13s7p4d3f2g); Dolg (1995).

^e Quasirelativistic 29 and 43 valence electron pseudopotentials for Ac and Lr, respectively. Basis sets: Ac, Lr (12s11p10d8f2g)/[8s7p6d5f2g], H (5s2p1d)/[3s2p1d], O, F (10s5p2d1f)/[4s3p2d1f]; Küchle et al. (1995)

^f Dolg et al. (1989c, 1991b).

^g Wang and Schwarz (1995).

^h Pyykkö and Desclaux (1977, 1979b).

Pyykkö (1979b) used the Dirac-Hartree-Fock one-centre expansion method for the monohydrides to calculate relativistic values for the lanthanide and actinide contraction, i.e. 0.209 Å for LaH to LuH and 0.330 Å for AcH to LrH. The corresponding nonrelativistic value derived from Hartree-Fock one-center expansions for LaH and LuH is 0.191 Å, i.e., for this case 9.4% of the lanthanide contraction is due to relativistic effects. The experimental value of 0.179 Å would suggest a correlation contribution of -14.4% to the lanthanide contraction if one assumes that the relativistic theoretical values are close to the Dirac-Hartree-Fock limit, which is certainly not true for the absolute values of the bond lengths themselves. Moreover, it is well known that for heavy elements relativistic calculations for AcH and LrH have not been performed and experimental data are not available to determine relativistic and electron correlation effects for the actinide contraction. Table 8 summarizes values for the lanthanide and actinide contraction derived from theoretical or experimental molecular bond lengths. It is evident from these results

Method ^a	Atom		ε (a.u.)			$\langle r \rangle$ (a.u.)		
		nd _{3/2}	nd _{5/2}	$(n+1)s_{1/2}$	nd _{3/2}	nd _{5/2}	$(n+1)s_{1/2}$	
HF	pseudo-Au ^b	0.5372	0.5372	0.1905	1.7228	1.7228	4.2230	
	pseudo-111 E°	0.4985	0.4985	0.1839	1.9933	1.9933	4.4359	
	Au ^b	0.5210	0.5210	0.2208	1.5433	1.5433	3.7006	
	111 E °	0.5243	0.5243	0.2010	1.7434	1.7434	4.0524	
DHF	pseudo-Au ^c	0.5152	0.4793	0.2210	1.7252	1.7730	3.7777	
	pseudo-111E°	0.4497	0.3850	0.2929	2.0061	2.1287	3.3101	
	Au ^b	0.4935	0.4287	0.2917	1.5359	1.6185	3.0609	
	111 E °	0.4649	0.3590	0.4202	1.7339	1.9094	2.6215	
HF	pseudo-Hg ^b	0.7191	0.7191	0.2288	1.6040	1.6040	3.7500	
	pseudo-112 E°	0.6474	0.6474	0.2174	1.8725	1.8725	3.9911	
	Нg ^ь	0.7142	0.7142	0.2610	1.4327	1.4327	3.3284	
	112 E°	0.6474	0.6474	0.2174	1.8725	1.8725	3.9911	
DHF	pseudo-Hg°	0.6771	0.6348	0.2586	1.6082	1.6488	3.4233	
	pseudo-112 E°	0.5542	0.4794	0.3226	1.8924	1.9997	3.1158	
	Hg⁵	0.6501	0.5746	0.3280	1.4312	1.4987	2.8434	
	112 E°	0.5627	0.4420	0.4513	1.6430	1.7951	2.4985	

Table 9

Negative valence orbital energies and radial expectation values of the atoms Au, Hg (n=5), 111 E and 112 E (n=6) and the corresponding 'pseudo-atoms' without the 4f or 5f shell and with a nuclear charge diminished by 14

^a Methods: HF, Hartree-Fock;

DHF. Dirac-Hartree-Fock.

^b Bagus et al. (1975).

```
° Seth et al. (1995).
```

that it is not possible to extract a common value for the lanthanide or actinide contraction. As will be discussed later the relatively small value of 0.04 Å for the lanthanide monoxides results from a f-orbital participation to bonding in LaO, whereas the 4f shell has core character in LuO. It might be expected that the values also depend on the electronic state for a given type of molecule. In a recent publication Wang and Schwarz (1995) point out that in addition the 'rigidity' of the bond is important. Compounds with 'rigid' bonds (large force constants, large bond energies) like RO (force constant $k \approx 5$ N/cm) will undergo only a small lanthanide contraction, whereas for those with 'soft' bonds like RH ($k \approx 1$ N/cm) one finds a large lanthanide contraction. RF compounds ($k \approx 3$ N/cm) are intermediate cases.

The influence of relativity and the filling of the 4f shell, i.e. the lanthanide contraction, on the 5d transition metals has been investigated by Bagus et al. (1975). Corresponding work for the 3d shell, i.e. the transition metal contraction, is due to Pyykkö (1979c). Similar investigations of the influence of the actinide contraction for the superheavy 6d transition metals have recently been carried out by Seth et al. (1995). The idea behind this work is that a shell-structure effect like the filling of the 4f or 5f shell may be separated from the relativistic effects due to the increasing nuclear charge by considering so-called 'pseudo-atoms' in the transition series, where the 4f or 5f shell is missing and the nuclear



Fig. 6. Orbital energies of valence s orbitals for group 11 and 12 metals. DHF and HF refer to Dirac-Hartree-Fock and Hartree-Fock results, respectively; p denotes calculations for the pseudoatoms where the effect of the 4f shell (Au, Hg) and 5f shell ($_{111}$ E, $_{112}$ E) has been omitted. Data taken from Bagus et al. (1975) and Seth et al. (1995).

charge has been reduced by 14 atomic units, i.e. the pseudo-Lu and pseudo-Lr atoms are La and Ac, respectively. Some results for orbital energies and radial expectation values for ₇₉Au, ₈₀Hg, ₁₁₁E, ₁₁₂E as well as the corresponding 'pseudo-atoms' have been summarized in table 9 and fig. 6. Clearly, this method allows only an approximate separation of relativistic and shell structure effects, which are not additive. If one looks at the sequence HF,p–HF–DHF for ₁₁₁E and ₁₁₂E one concludes that only relativity causes the stabilization of the 7s shell, whereas the series HF,p–DHF,p–DHF suggests that actinide contraction and relativistic Dirac–Hartree–Fock calculations, respectively; HF,p and DHF,p stand for the corresponding calculations using pseudo-atoms.)

It should be noted that for $_{111}$ E only the $[_{86}Rn]5f^{14}6d^{10}7s^1$ configuration was considered, whereas at the Dirac–Hartree–Fock level a $[_{86}Rn]5f^{14}6d^97s^2$ ground state configuration is obtained due to the strong destabilization of the 6d orbitals by dominating indirect relativistic effects (Seth et al. 1995). Large-scale coupled-cluster calculations based on the Dirac–Coulomb–Breit Hamiltonian with up to h functions in the basis set also give a $[_{86}Rn]5f^{14}6d^97s^2$ $^2D_{5/2}$ ground state (Eliav et al. 1994b). The $[_{86}Rn]5f^{14}6d^97s^2$ $^2D_{3/2}$ and $[_{86}Rn]5f^{14}6d^{10}7s^{12}S_{1/2}$ excited states have term energies of 2.69 eV and 2.95 eV, respectively.

1.4. The superconfiguration model

The superconfiguration (SC) model proposed by Field (1982) for the lanthanide monoxides proved to be very useful for the interpretation of the complex spectra of these

molecules. According to Field the electron configuration of a lanthanide monoxide may be partitioned into a chemically completely inactive core electron system $(R^{(n+3)+}[Xe])$ $O^{4+}1s^22s^2$), a usually only partially occupied 4f subshell with n or n+1 electrons and a valence electron configuration with 7 or 6 electrons in σ , π and δ orbitals formed by the R 5d, 6s, 6p and O 2p atomic orbitals. The numbering n=0-14 for the elements La-Lu will be used throughout this article, i.e., n denotes the f orbital occupation number for the ground-state configuration of the ions R^{3+} . Whereas the valence electron system has to be treated by molecular orbital theory, the atomic-like 4f subshell may be treated by ligand field theory. All electronic states that belong to a given valence substate and a specific 4f subconfiguration are said to belong to a SC. States that arise from the same SC are assumed to have almost identical spectroscopic constants which are determined by the valence substate, whereas the different couplings within the 4f subconfiguration and between the resulting 4f substate and the valence substate cause only minor deviations. The basic assumption is that the 4f orbitals do not directly participate in chemical bonding in a molecular orbital sense. However, indirect effects of the 4f shell may be present, e.g. when the atomic and molecular ground states have different 4f subconfigurations and a corresponding rearrangement has to take place upon formation of a molecular bond. In addition, the 4f shell considerably contributes to the complexity of the electronic spectra of lanthanide compounds. Field (1982) proposed that the ground states of the lanthanide monoxides arise from the SC

 $[R 4f^{n}] \sigma^{2}_{O2p} \pi^{4}_{O2p} \sigma^{1}_{R6s,6p}$

for LaO to SmO, TbO to TmO and LuO. In two cases, EuO and YbO, a half-filled or filled 4f subshell can be achieved by promoting one electron from the $\sigma_{R6s,6p}$ orbital to the subshell, and the ground states should arise from the SC

$$[R 4f^{n+1}] \sigma^2_{O2p} \pi^4_{O2p}.$$

For reasons of brevity and in cases where no confusion can arise we will omit R, the brackets as well as the subscripts on the valence orbitals, e.g. we write $4f^n\sigma^2\pi^4\sigma^1$ and $4f^{n+1}\sigma^2\pi^4$ for the two SCs given above.

The SC model may also be applied successfully to other lanthanide compounds, e.g. the monofluorides (Gotkis 1991). The model was used as basic idea for a simple combined pseudopotential and ligand field approach for the lanthanides by the present authors (Dolg 1989, Dolg et al. 1989b,c, 1993a, Dolg and Stoll 1989). The 4f shell was attributed to the pseudopotential core and not treated explicitly in the calculations which yield results for a specific SC. Divalent ($4f^{n+1}$), trivalent ($4f^n$) and tetravalent ($4f^{n-1}$) lanthanide atoms are expected to behave roughly like Ca, Sr, Ba (divalent), Sc, Y, La (trivalent) and Ti, Zr, Hf (tetravalent) atoms, respectively. Results for individual states arising from the open 4f subshell may be derived from a subsequent ligand field model calculation. Clearly, the model is bound to fail whenever the 4f orbitals mix considerably with the valence orbitals, e.g. for CeO₂ (Dolg 1995) where the bond angle is essentially determined by

the relative importance of 4f- and 5d-orbital participation or for Ce @ C_{28} (@ denotes a Ce atom inside the C_{28} cage) where the 4f orbitals participate in metal-cage bonding (Rösch et al. 1993). There are also cases where the hybridization between the 4f and the other valence orbitals is small, however mixing between configurations with different 4f occupations is important even in the zeroth-order wavefunction, e.g. for the ground states of YbO (Dolg et al. 1992c, Wang and Schwarz 1995) and cerocene, Ce(C₈H₈)₂ (Dolg et al. 1991d, 1995).

2. Methods

Special relativity (Einstein 1905) and quantum mechanics (Heisenberg 1925, Schrödinger 1926) provide the fundamental concepts for relativistic heavy-element chemistry and physics. A suitable starting point for a rigorous theoretical derivation of a relativistic many-electron theory is quantum electrodynamics (QED) (Bethe and Salpeter 1957, Itzykson and Zuber 1980). In order to derive the working equations one has in a first step to decouple the field of electrons and positrons from that of photons, and in a second step the electronic field from the positronic field. Unfortunately, neither of these two steps can be carried out in closed form without approximations (Kutzelnigg 1987). Therefore, the resulting relativistic many-electron Hamiltonians published in literature so far are at most correct only to order α^2 (fine-structure constant $\alpha = 1/c$; velocity of light c = 137.0359895 a.u. according to the 1987 adjustment of fundamental constants summarized, e.g., by Cohen and Taylor 1987). The question which specific relativistic many-electron Hamiltonian to choose for all-electron calculations in atomic structure theory or quantum chemistry still seems not to be fully settled.

We will therefore base our discussion on a general Hamiltonian for a molecule with n electrons and N nuclei formulated within the Born–Oppenheimer approximation (Born and Oppenheimer 1927), and restrict it to one- and two-particle terms,

$$\mathcal{H} = \sum_{i}^{n} h(i) + \sum_{i < j}^{n} g(i, j) + \sum_{\lambda < \mu}^{N} \frac{Z_{\lambda} Z_{\mu}}{r_{\lambda \mu}}.$$
(8)

The indices i, j denote electrons, whereas λ, μ stand for nuclei with charges Z_{λ} and Z_{μ} . Relativistic, quasirelativistic or nonrelativistic expressions may be inserted into this Hamiltonian for the one- and two-electron operators h and g, respectively. In some cases, e.g. the relativistic all-electron Dirac–Coulomb–(Breit/Gaunt) Hamiltonian, it is necessary to (formally) bracket the Hamiltonian by projection operators onto many-electron (positive energy) states in order to avoid problems connected with unwanted many-electron–positron (negative energy) states.

The stationary states of the atom or molecule fulfill the time-independent Schrödinger equation

$$\mathcal{H}\Psi = E\Psi.\tag{9}$$

However, except for the simplest one-electron systems, only approximate solutions of this equation may be obtained. Since the correct form of the relativistic many-electron Hamiltonian is not known and, as for the nonrelativistic case, further approximations have to be introduced in the wavefunction, it is tempting to derive approximate computational schemes which are still sufficiently accurate but more efficient. Here we will only summarize those approximate methods that have been used frequently to obtain information about the electronic structure of molecules with lanthanide atoms, i.e. relativistically corrected density-functional approach, pseudopotential method, intermediate neglect of differential overlap method, extended Hückel theory, and ligand field theory.

2.1. All-electron methods

All-electron (AE) calculations are certainly the most rigorous way to treat atoms and molecules, however, the computational requirements are sometimes prohibitive, especially for molecular Dirac–Hartree–Fock–Roothaan (DHFR) and subsequent configuration interaction (CI) calculations. Nevertheless, very accurate all-electron calculations on small systems yield important reference data for the calibration of more approximate computational schemes, e.g. valence-electron (VE) methods, which may be applied to larger systems.

Significant progress has been made during the last few years to develop the methods of relativistic quantum chemistry parallel to the existing nonrelativistic approaches. A key step was the development of a reliable DHFR scheme using kinetically balanced basis sets. Currently several of the existing relativistic electronic structure codes are extended to electron correlation as well. It might be hoped that in view of the fast developments in computer technology calculations of reasonable accuracy for small molecules with one or two heavy elements become feasible until the end of the century. At the present stage the accurate treatment of electron correlation seems to be the bottleneck for such investigations rather than the treatment of relativity.

2.1.1. Dirac-Coulomb-(Breit/Gaunt) Hamiltonian

A quite rigorous and practicable approach for electronic structure calculations of atoms and molecules is based on the Dirac-Coulomb Hamiltonian, i.e., the exact relativistic Dirac Hamiltonian (Dirac 1928a,b, 1929) is used for the one-electron terms (the rest energy has been subtracted),

$$h_{\rm D}(i) = c \,\boldsymbol{\alpha}_i \boldsymbol{p}_i + (\boldsymbol{\beta}_i - \mathbf{I}_4) \, c^2 + \sum_{\lambda} \, V_{\lambda}(r_{i\lambda}), \tag{10}$$

and the nonrelativistic Coulomb interaction for the two-electron terms

$$g_{\rm C}(i,j) = \frac{1}{r_{ij}}.$$
 (11)

Here c denotes the velocity of light, I_4 the 4×4 unit matrix and $p_i = -i\nabla_i$ is the momentum operator for the *i*th electron. α_i is a three-component vector; together with

 β_i its components form the 4×4 Dirac matrices acting on the *i*th electron. α may be formulated in the standard representation in terms of the three 2×2 Pauli spin matrices $\sigma^{\rm P} = (\sigma_x^{\rm P}, \sigma_y^{\rm P}, \sigma_z^{\rm P})$, and β in terms of the 2×2 identity matrix I₂,

$$\boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & 0\\ 0 & -\mathbf{I}_2 \end{pmatrix} \qquad \boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma}^{\mathrm{P}}\\ \boldsymbol{\sigma}^{\mathrm{P}} & 0 \end{pmatrix}$$
(12)

with

$$\boldsymbol{\sigma}_{x}^{\mathrm{P}} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \boldsymbol{\sigma}_{y}^{\mathrm{P}} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \boldsymbol{\sigma}_{z}^{\mathrm{P}} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$
(13)

 $V_{\lambda}(r_{i\lambda})$ is the electrostatic potential for the *i*th electron due to the charge distribution of nucleus λ . The simplest choice is to approximate the nucleus as a point charge Z_{λ} , i.e.,

$$V_{\lambda}(r_{i\lambda}) = -\frac{Z_{\lambda}}{r_{i\lambda}}.$$
(14)

The point charge model is sufficiently accurate if one is interested in valence properties of atoms and molecules, however, more realistic finite nucleus models may be used instead. In recent years a Gaussian nuclear charge distribution (Visser et al. 1987),

$$\rho_{\lambda}(r) = \rho_{\lambda}^{0} \exp(-\eta_{\lambda} r^{2}) \quad \text{with} \quad 4\pi \int_{0}^{\infty} \mathrm{d}r \, r^{2} \rho_{\lambda}(r) = Z_{\lambda}, \tag{15}$$

has become quite popular due to the simplicity of the resulting one-particle integrals when cartesian Gaussian basis sets are used. The parameter η_{λ} can be related to the nuclear radius R_{λ} or the atomic mass M_{λ} :

$$\eta_{\lambda} = \frac{3}{2R_{\lambda}^2}$$
 with $R_{\lambda} = 2.2677 \times 10^{-5} M_{\lambda}^{1/3} a_0.$ (16)

A practical advantage of the finite-nucleus model is that extremely high exponents of the one-particle basis functions are avoided. Since for quantities of chemical interest it is not very important which nuclear model is actually used, the Gaussian charge distribution is often applied, being the most convenient choice.

Although in the Dirac–Coulomb Hamiltonian the one-particle operator is correct to all orders in α , the two-particle interaction is only correct to α^0 . The Dirac–Coulomb Hamiltonian is not invariant under Lorentz transformations, however it can be considered as the leading term of a yet unknown relativistic many-electron Hamiltonian which fulfills this requirement. An operator which also takes into account the leading relativistic corrections for the two-electron terms is the Coulomb–Breit term (Breit 1929, 1930, 1932, 1938),

$$g_{\rm CB}(i,j) = \frac{1}{r_{ij}} - \frac{1}{2r_{ij}} \left[\boldsymbol{\alpha}_i \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \boldsymbol{r}_{ij})(\boldsymbol{\alpha}_j \boldsymbol{r}_{ij})}{r_{ij}^2} \right].$$
(17)

The resulting Dirac–Coulomb–Breit many-electron Hamiltonian is now correct to order α^2 . The Breit interaction can be rewritten as a sum of two terms: the magnetic interaction

and the retardation of the interaction due to the finite velocity of light. The corresponding radiation process is the emission of a single virtual transverse photon by one electron and its absorption by the other electron. (When the emitting electron is identical to the absorbing electron the self-interaction results in the Lamb shift which is of the order $\alpha^3 Z \log \alpha$.) Often only the leading magnetic interaction is considered, i.e. the Coulomb-Gaunt term (Gaunt 1929a,b),

$$g_{\rm CG}(i,j) = \frac{1}{r_{ij}} - \frac{\alpha_i \alpha_j}{r_{ij}}.$$
(18)

Since there are no additional two-particle integrals to evaluate when the Gaunt term is included in the Hamiltonian, the calculation of the magnetic interaction affords almost no additional costs. This is not the case for the retardation term, which usually yields energetic contributions of 10% compared to the magnetic part and therefore is often neglected. Several studies on heavy-element compounds showed that for quantities of chemical interest like bond lengths, vibrational frequencies or binding energies the Dirac–Coulomb Hamiltonian is sufficiently accurate (Pyykkö 1978, Visser et al. 1992a). Moreover, contributions of electron correlation can be expected to be usually far more important for the calculation of these quantities than the Breit or Gaunt interaction.

Due to the presence of the one-particle Dirac operators which allow for positronic and electronic solutions at negative and positive energies, respectively, all resulting many-electron Hamiltonians are not bounded from below, and there are no stable many-electron solutions if not additional precautions are taken. The restriction to the interesting many-electron solutions is possible by means of the Dirac-Hartree-Fock (DHF) method (Hartree 1929, Gaunt 1929b, Swirles 1935, 1936), which is designed quite similarly as the nonrelativistic Hartree-Fock (HF) method (Hartree 1928a,b, 1957, Slater 1929, Fock 1930). The many-electron wave function Ψ is approximated as a configuration state function (CSF) which satisfies the eigenvalue equations of symmetry-related operators commuting with the Hamiltonian, e.g. the angular momentum and parity operators for an atom or symmetry operators of the relevant double point group for a molecule. In general a CSF has to be written as a linear combination of a minimum number of antisymmetrized products ϕ of orthonormal one-particle functions φ (Slater determinants, configurations) fulfilling these requirements, i.e.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \sum_I C_I \Phi_I(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$
(19)

with

$$\Phi_{I}(\mathbf{r}_{1},\mathbf{r}_{2},\ldots,\mathbf{r}_{n}) = \frac{1}{\sqrt{n!}} \det(\phi_{I1}(\mathbf{r}_{1}),\phi_{I2}(\mathbf{r}_{2}),\ldots,\phi_{In}(\mathbf{r}_{n})).$$
(20)

In contrast to the nonrelativistic HF scheme the one-particle functions are now fourcomponent spinors (instead of spin-orbitals or orbitals) containing an upper and a lower bispinor as components. Since the contribution to the norm of the upper bispinor is usually large for electrons, it is frequently called 'large' component, whereas the lower bispinor is referred to as the 'small' component. In the DHF formalism one seeks to obtain stationary values of the total energy functional

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle \tag{21}$$

with respect to a variation of the one-particle functions ϕ under the condition that they still form an orthonormal set. The resulting DHF equations

 $\mathcal{F}_{\rm DHF}\phi = \varepsilon\phi \tag{22}$

may be solved either by finite difference methods or by algebraic, i.e. finite basis set expansion methods. Since the DHF operator \mathcal{F}_{DHF} depends on the occupied one-particle functions the solution of the resulting integrodifferential or matrix eigenvalue equations has to be found iteratively using the self-consistent field (SCF) procedure. In contrast to the nonrelativistic HF method the ground state of a many-electron system is now not obtained by occupying in each iteration the one-particle solutions lowest in energy, but rather the energetically lowest solutions belonging to the positive energy spectrum. This selection of occupied one-particle functions avoids the so-called 'variational collapse' (Schwarz and Wallmeier 1982) which may occur due to the unboundedness of the Dirac Hamiltonian from below. Upon convergence of the SCF procedure one gets a division of the space of one-particle functions into negative-energy (positronic) and positive-energy (electronic) solutions.

For atoms one usually applies the central-field approximation, and the four-component spinors are written as

$$\phi_{n\kappa m}(r,\vartheta,\varphi) = \frac{1}{r} \begin{bmatrix} P_{n\kappa}(r) \chi_{\kappa m}(\vartheta,\varphi) \\ iQ_{n\kappa}(r) \chi_{-\kappa m}(\vartheta,\varphi) \end{bmatrix}.$$
(23)

 $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ denote the radial parts for the upper and lower components, respectively. The corresponding angular parts consist of two-component spinor spherical harmonics

$$\chi_{\kappa m}(\vartheta, \varphi) = \sum_{\sigma = \pm 1/2} C(l_2^{1}j; m - \sigma, \sigma) Y_l^{m - \sigma}(\vartheta, \varphi) \phi_{1/2}^{\sigma}, \qquad (24)$$

which are given in terms of the Clebsch-Gordan coefficients $C(l_2^1 j; m - \sigma, \sigma)$, the spherical harmonics $Y_l^{m-\sigma}(\vartheta, \varphi)$ and the two-component Pauli spinors $\phi_{1/2}^{\sigma}$, i.e.,

$$\phi_{1/2}^{1/2} = \begin{pmatrix} 1\\ 0 \end{pmatrix}$$
 and $\phi_{1/2}^{-1/2} = \begin{pmatrix} 0\\ 1 \end{pmatrix}$. (25)

The relativistic quantum number κ is defined as

$$\kappa = \pm \left(j + \frac{1}{2}\right) \quad \text{for} \quad j = l \mp \frac{1}{2}.$$
(26)

Starting from the Dirac-Coulomb Hamiltonian and a single Slater determinant as many-electron wavefunction Swirles (1935, 1936) derived the relativistic DHF equations

for a closed-shell atom in analogy to the nonrelativistic HF equations (Hartree 1928a,b, 1957, Fock 1930) by application of a variational principle to the energy functional. A pair of radial functions $P_{n\kappa}(r)$, $Q_{n\kappa}(r)$ for a bound one-particle state ($\varepsilon_{n\kappa} < 0$) may be obtained by solving radial equations of the following type:

$$\frac{\mathrm{d}}{\mathrm{d}r} \begin{bmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{bmatrix} = \begin{bmatrix} -X_{n\kappa}^{P}(r)/r \\ X_{n\kappa}^{Q}(r)/r \end{bmatrix} +$$
(27)

$$\begin{bmatrix} -\kappa/r & (2/\alpha) + \alpha[\varepsilon_{n\kappa} - Y_{n\kappa}(r)/r] \\ -\alpha[\varepsilon_{n\kappa} - Y_{n\kappa}(r)/r] & \kappa/r \end{bmatrix} \begin{bmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{bmatrix}.$$
 (28)

The DHF problem was later reformulated by Grant (1961) using Racah's tensor operators (Racah 1942a,b, 1943, 1949) and extended to open-shell systems. The derivation of the more general multi-configuration DHF (MCDHF) equations follows the lines known from the nonrelativistic multi-configuration HF (MCHF) approach. Today the approximate solution of the atomic many-electron problem is routinely obtained using finite-difference methods, whereas the angular parts are treated analytically. Usually the Dirac-Coulomb Hamiltonian is used during the SCF procedure, and the corrections due to the Breit interaction and the quantum electrodynamic effects like the self-energy of the electron and the vacuum polarisation are added in perturbation theory. Mann and Johnson (1971) investigated the contribution of the Breit interaction to the total ground state energy of many-electron atoms. It was found that the DHF energy behaves approximately as $Z^{2.4}$, whereas the magnetic and retardation contributions increase as $Z^{3.6}$. The corresponding computer programs have been developed and are available, e.g. Desclaux (1975, 1977), Grant et al. (1980) or Dyall et al. (1989). For further details on the finite-difference DHF and MCDHF methods we refer to the articles by Grant (1961, 1970, 1983a-d, 1984, 1986, 1988), Lindgren and Rosén (1974), Desclaux (1983a) or Grant and Quiney (1988). Information on the corresponding nonrelativistic methods and programs may be obtained from the book of Froese Fischer (1977) and in the publications describing their newest program system (Froese Fischer 1991a-c, Froese Fischer and Liu 1991, Froese Fischer and Godefroid 1991, Hibbert and Froese Fischer 1991, Hibbert et al. 1991).

Early results for relativistic calculations on molecules with a single heavy atom and preferably hydrogen ligands have been obtained by Desclaux and Pyykkö (1974, 1976) (cf. also Desclaux 1983b) using the one-center-expansion technique originally developed by Mackrodt (1970). Although the results are poor due to the limited basis set and the complete neglect of electron correlation, these calculations gave a first insight into relativistic effects for heavy-element compounds; for instance, the relativistic bond-length contraction (Desclaux and Pyykkö 1974, 1976), the relativistic contributions to the lanthanide contraction (Pyykkö 1979b) or the effects of higher-order relativistic corrections to the Coulomb interaction (Pyykkö 1978) could be investigated.

A more recent development are DHF or MCDHF programs based on the algebraic approximation, i.e. finite basis set expansions are used instead of finite difference methods, cf. e.g. Grant and Quiney (1988). The first work on closed and open shell atoms was published by Kim (1967) and Kagawa (1975), respectively. Nevertheless these algebraic

methods are mainly developed with a possible extension of relativistic all-electron calculations to molecules in mind: in analogy to Roothaan's SCF MO-LCAO (molecular orbitals by linear combination of atomic orbitals) approach (Roothaan 1951, 1960) which is definitely one of the most successful concepts in nonrelativistic computational chemistry, the basic equations of a relativistic SCF MS-LCAS (molecular spinors by linear combination of atomic spinors) theory have been written down for closed and open shell systems by Malli and Oreg (1975) and Malli (1980), respectively. Matsuoka et al. (1980) proposed a MCSCF (multi-configuration self-consistent field) scheme for closed shell molecules. Several finite basis set codes to perform such molecular Dirac-Hartree-Fock-Roothaan (DHFR) calculations are available (Malli 1983b, 1994b, Aerts 1986, Aerts and Nieuwpoort 1986a,b, Malli and Pyper 1986, Wilson 1988b, Dyall et al. 1991, Mohanty and Clementi 1991, Baeck and Lee 1994, Dyall 1994a, DeJong et al. 1994, Nieuwpoort et al. 1994). The Gaunt or Breit interaction can also be taken into account (Rosicky 1982, Baeck and Lee 1994, DeJong et al. 1994). The SCF MS-LCAS method also forms a good starting point for atomic and molecular calculations that include electron correlation effects, e.g. by subsequent MRCI calculations as has been shown by Esser et al. (1981), Esser (1983, 1984a,b) or more recently by Visscher (1993) and Visscher et al. (1993, 1994). An MP2 code has been developed by Dyall (1994c). For atoms a DHFR and coupled-cluster (CC) code exists (Ishikawa 1990, Eliav et al. 1994a). The relativistic many-body perturbation theory also has been developed (Quiney 1988, Wilson 1988b), and a MRPT (multi-reference perturbation theory) extension of Esser's MRCI code exists (Dolg 1995). Early attempts to perform DHF calculations using finite basis sets (Mark et al. 1980, Mark and Rosicky 1980) have often been plagued by the so-called 'finite basis set disease' (Schwarz and Wechsel-Trakowski 1982). The problems were mostly due to the fact that the relation between the upper, ϕ^{U} , and lower, ϕ^{L} components of a Dirac solution

$$\phi^{\rm L} = \frac{c}{V - \varepsilon - 2c^2} \, \boldsymbol{\sigma} \boldsymbol{p} \phi^{\rm U} \tag{29}$$

have been disregarded when chosing the one-particle basis set, thus leading to a wrong matrix representation of the kinetic energy (Schwarz and Wechsel-Trakowski 1982, Schwarz and Wallmeier 1982, Mark and Schwarz 1982). If, in the worst case, the small component basis is omitted, a zero kinetic energy results and the potential energy remains unbalanced, thus yielding too low one-particle energies. We note that the 'finite basis set disease' (occupation of low- or zero-kinetic energy one-electron states) has to be distinguished from the 'variational collapse' (occupation of positronic states), although they are related by the unboundedness of the Dirac Hamiltonian from below and their practical consequences (too low total energies) are the same. The so-called 'kinetic balance condition' (Stanton and Havriliak 1984) is an approximation of this relation

$$\phi^{\rm L} = \frac{-1}{2c} \boldsymbol{\sigma} \boldsymbol{p} \phi^{\rm U} \tag{30}$$

and leads to a simple prescription for avoiding the 'finite basis set disease'. Primitive basis functions used in the scalar basis for the upper component must have a function resulting

from the application of this condition in the basis for the lower component. Other forms of balance between the upper and lower components of a spinor basis are discussed, e.g., in an article by Nieuwpoort et al. (1994). A modified matrix representation of the relativistic kinetic energy has been proposed by Mark and Schwarz (1982).

In order to go beyond the DHF approach, e.g. to include electron correlation effects by means of configuration interaction methods, the positronic one-particle states are discarded and the many-electron basis is constructed using only the electronic one-particle states, i.e., the one- and two-particle integrals are transformed from the atomic spinor basis set to the molecular spinor basis set using only the positive-energy one-particle DHF solutions. This prescription avoids the so-called 'Brown–Ravenhall disease' (Brown and Ravenhall 1951) or 'continuum dissolution' (Sucher 1983, 1984), i.e. an unphysical mixing of unwanted configurations with simultaneously occupied positron and electron one-particle states and the desired configurations with only occupied electron one-particle states. The 'continuum dissolution' is a consequence of the unboundedness of the Dirac Hamiltonian which shows up only for many-electron systems. In a certain sense the selection of the positive-energy spinor space from the DHF calculations may be viewed to have the same effect as a projection operator on many-electron states bracketing the Hamiltonian.

A review of the problems associated with the Dirac Hamiltonian as well as a classification of attempts to avoid them has been given by Kutzelnigg (1984). Recently, the same author developed a direct perturbation theory for relativistic effects (Kutzelnigg 1990, Kutzelnigg et al. 1995, Ottschofski and Kutzelnigg 1995). Earlier work in this direction was published by Rutkowski (1986a–c) and Jankowski and Rutkowski (1987). A modification of the Dirac–Coulomb–Breit Hamiltonian which allows the exact separation of spin-free and spin-dependent terms has been proposed by Dyall (1994b).

2.1.2. Douglas-Kroll-Hess Hamiltonian

DHF calculations on molecules using finite basis sets require considerably more computational effort than the corresponding nonrelativistic calculations and cause several problems due to the presence of the Dirac one-particle operator. It is therefore desirable to find (approximate) relativistic Hamiltonians for many-electron systems which are not plagued by unboundedness from below and therefore do not cause problems like the 'variational collapse' at the self-consistent field level or the 'Brown-Ravenhall disease' at the configuration interaction level. It is also desirable to find forms in which the quality of a matrix representation of the kinetic energy is more stable than for the Dirac Hamiltonian, i.e., forms which are not affected by the 'finite basis set disease'.

The Foldy-Wouthuysen transformation (FWT) (Foldy and Wouthuysen 1950) of the Dirac Hamiltonian uses a sequence of unitary operators $U = \exp(iS)$, with S being hermitian, to decouple the upper from the lower components of the wavefunction $\Psi' = U \Phi$ and to remove odd terms in the resulting Hamiltonian $\mathcal{H}' = U\mathcal{H}U^{-1}$ successively up to a given order of α^2 . (Odd operators like α couple the upper and lower components, whereas even operators like β do not; if the resulting Hamiltonian is even up to a given order of α^2 , its

part acting on the upper components may be used as a quasirelativistic Hamiltonian for electrons.) The nonrelativistic Hamiltonian is obtained as the leading term with order α^0 . The most important relativistic one-particle correction terms with order α^2 are the mass– velocity, Darwin and spin–orbit terms of the Pauli equation resulting from the first FWT of the Dirac Hamiltonian. The corresponding FWT of the Dirac–Coulomb–Breit Hamiltonian yields the Breit–Pauli operator (Itoh 1965). Unfortunately some terms in the Pauli and Breit–Pauli Hamiltonian are highly singular and are not suitable for a variational treatment. Therefore these operators can only be used in first-order perturbation theory based on the nonrelativistic solutions of the many-electron problem, an approach which yields reasonable results for elements as heavy as silver, but certainly not for lanthanides, let alone actinides.

Douglas and Kroll (1974) modified the elimination of the positronic one-particle states in a way that leads to relativistic operators suitable for the variational approaches used in quantum chemistry. Instead of expansions in powers of α^2 the transformation is constructed to lead to expansions in powers of the external potential. The ideas of Douglas and Kroll were followed and implemented by Hess (1986), Jansen and Hess (1989a) and Samzow et al. (1992). Correct to second order in the potential the Douglas–Kroll–Hess (DKH) one-electron Hamiltonian is

$$h_{\text{DKH}}(i) = E_i + A_i \left[V(i) + \mathbf{R}_i V(i) \mathbf{R}_i \right] A_i - W_1(i) E_i W_1(i) - \frac{1}{2} \left\{ W_1(i)^2, E_i \right\},$$
(31)

where the braces denote an anticommutator, V is the external scalar potential and with

$$E_i = E_{p_i} = c\sqrt{p_i^2 + c^2}, \qquad A_i = A_{p_i} = \sqrt{\frac{E_i + c^2}{2E_i}}, \qquad R_i = \frac{\sigma_i p_i}{E_i + c^2}.$$
 (32)

The operator $W_1(i)$ is an integral operator with the kernel

$$W_{1}(\boldsymbol{p}, \boldsymbol{p}') = A_{p}(\boldsymbol{R}_{p} - \boldsymbol{R}_{p'})A_{p'}\frac{V(\boldsymbol{p}, \boldsymbol{p}')}{E_{p} + E_{p'}},$$
(33)

where V(p,p') denotes the Fourier transform of the external potential. The corresponding two-electron terms are

$$g_{\text{DKH}}(i,j) = A_i A_j \left[\frac{1}{r_{ij}} + R_i \frac{1}{r_{ij}} R_i + R_j \frac{1}{r_{ij}} R_j + R_i R_j \frac{1}{r_{ij}} R_i R_j \right] A_i A_j.$$
(34)

The DKH operator may be implemented in one-component form into standard quantum-chemistry codes and allows an accurate treatment of heavy-element atoms and molecules when the effects of spin-orbit coupling are negligible, e.g. Jansen and Hess (1989b), Chandra and Hess (1994), Gleichmann and Hess (1994), Kaldor and Hess (1994). The computational effort is only slightly higher than for the corresponding nonrelativistic calculations and the whole arsenal of methods for the correlation treatment

within nonrelativistic coupling schemes (LS or $\Lambda\Sigma$ coupling for atoms and linear molecules, respectively) are at hand once the one-electron integral routines have been modified. A local density-functional approach using the DKH Hamiltonian has been developed by the group in Munich (Rösch and Häberlen 1992, Häberlen and Rösch 1992). A spin-orbit operator may also be derived for the DKH formalism and was used for calculations on transition-metal compounds, e.g. Fleig and Marian (1994). In this two-component form the DKH approach might become suitable for investigations of lanthanide and actinide systems in the near future.

It is worth mentioning that there has been quite a number of attempts to derive well-behaved relativistic Hamiltonians for all-electron calculations, e.g. Wallmeier and Kutzelnigg (1981), Almloef et al. (1985), C. Chang et al. (1986), Heully et al. (1986), Schwarz and Kissel-Phillip (1988) or Van Lenthe et al. (1993, 1994). To our knowledge none of these approaches has been applied so frequently and successfully for molecular calculations as the DKH Hamiltonian. The recent work of Van Lenthe et al. appears to be especially promising in the case of density-functional methods.

2.1.3. Cowan-Griffin and Wood-Boring schemes

Cowan and Griffin (1976) developed an approximate one-component guasirelativistic extension of the HF method, which in the literature is sometimes referred to as HFR (Martin and Hay 1981) method (HF with relativistic corrections), for numerical calculations on atoms within the LS-coupling scheme. The method, which is hereafter referred to as the Cowan–Griffin scheme (CG), obtains approximate relativistic corrections by adding energy-dependent terms corresponding to order α^2 to the mass-velocity and Darwin term of the Pauli equation for a one-electron atom to the HF differential equations. The need for the application of the jj-coupling scheme, and therefore a two-component formalism, was avoided by omitting a term corresponding to the spin-orbit term of the Pauli equation. Cowan and Griffin showed that even for atoms as heavy as uranium the major relativistic effects besides spin-orbit coupling, both direct and indirect, are reproduced to good accuracy by their method. The results derived from the self-consistent quasirelativistic CG treatment were far superior to those obtained by the application of first-order perturbation theory for quasirelativistic operators to the nonrelativistic HF wavefunction. Since for most of the low-lying electronic states of the lighter elements the coupling scheme is closer to LS- than to jj-coupling, the CG method became quite popular. It was used by Martin and Hay (1981) to investigate differential relativistic and correlation effects in excitation and ionization energies of transition metals, i.e. by comparing HF to CG, and CG to spin-orbit averaged experimental values, respectively. An approximate extension of the CG method to molecules was investigated by Martin (1983), although his approach may also be viewed as perturbational treatment of the mass-velocity and Darwin terms of the Pauli equation for SCF wavefunctions.

The CG method was first used by Kahn et al. (1978) for the uranium atom to obtain appropriate all-electron reference data for the generation of an ab initio pseudopotential which includes the major relativistic corrections except spin-orbit coupling. The latter effect can however be calculated using the scheme according to Blume and Watson (1962, 1963). The pseudopotential adjustment was performed with some necessary modifications similar to the nonrelativistic prescription given before by Kahn et al. (1976). Later Klobukowski (1983) modified Huzinaga's model potential method (Bonifacic and Huzinaga 1974, Sakai and Huzinaga 1982), taking the silver atom as an example, to allow for an approximate treatment of relativistic effects also starting from CG all-electron calculations. In the following years the CG scheme was applied by several groups in the course of the generation of one-component quasirelativistic ab initio pseudopotentials; see, e.g., the tables of effective core potentials (main group and transition metals) published by Hay and Wadt (1985a,b) and Wadt and Hay (1985) or those of model potentials (transition metals) given by Sakai et al. (1987a,b), Barandiarán et al. (1990) and Barandiarán and Seijo (1992).

The derivation of the working equations of the CG method starts with the radial Dirac equation for one particle in a central-field potential V(r), e.g. the local potential approximation to the DHF equations

$$\frac{\mathrm{d}}{\mathrm{d}r} \begin{bmatrix} P_{\mathrm{A}}(r) \\ Q_{\mathrm{A}}(r) \end{bmatrix} = \begin{bmatrix} -\kappa/r & (2/\alpha) + \alpha[\varepsilon_{\mathrm{A}} - V(r)] \\ -\alpha[\varepsilon_{\mathrm{A}} - V(r)] & \kappa/r \end{bmatrix} \begin{bmatrix} P_{\mathrm{A}}(r) \\ Q_{\mathrm{A}}(r) \end{bmatrix}.$$
(35)

Elimination of the small component $Q_A(r)$ leads to a second-order differential equation for the large component $P_A(r)$, the radial Wood–Boring (WB) equation (Wood and Boring 1978)

$$(\mathcal{H}_{\rm S} + \mathcal{H}_{\rm MV} + \mathcal{H}_{\rm D} + \mathcal{H}_{\rm SO})P_{\rm A}(r) = \varepsilon_{\rm A}P_{\rm A}(r) \tag{36}$$

in which

$$\mathcal{H}_{\rm S} = -\frac{1}{2} \frac{{\rm d}^2}{{\rm d}r^2} + \frac{l(l+1)}{2r^2} + V(r) \tag{37}$$

is the nonrelativistic Schrödinger Hamiltonian. The remaining three quasirelativistic operators are the mass-velocity, Darwin and spin-orbit terms

$$\mathcal{H}_{\rm MV} = -\frac{1}{2}\alpha^2 [\varepsilon_{\rm A} - V(r)]^2, \qquad \mathcal{H}_{\rm D} = -\frac{1}{4}\alpha^2 \frac{\mathrm{d}V}{\mathrm{d}r} B_{\rm A} \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r}\right), \tag{38}$$

$$\mathcal{H}_{\rm SO} = -\frac{1}{4}\alpha^2 \frac{\mathrm{d}V}{\mathrm{d}r} B_{\rm A} \frac{\kappa+1}{r}, \qquad B_{\rm A} = \frac{1}{1+\frac{1}{2}\alpha^2 [\varepsilon_{\rm A} - V(r)]}.$$
(39)

The WB equation is a two-component wave equation which for one-particle systems still yields the exact eigenvalues ε_A and the large component $P_A(r)$ of the Dirac equation. In order to get to a two-component quasirelativistic formalism one has to neglect the small components and to assume the large ones to be normalized to unity. It should be noted that, due to the energy dependency of the quasirelativistic operators, spinors
of equal quantum number κ are not orthogonal onto each other. The necessity to work with nonorthogonal spinors was closer investigated by Kobus (1986) who performed test calculations for the $1s^22s^22p^1$ configuration of U^{87+} .

The desired switch from jj-coupling to LS-coupling was obtained by Cowan and Griffin (1976) by simply neglecting the spin-orbit and Darwin terms for $l \ge 1$. Two objections may be raised against this approximation. First, due to neglect of the Darwin term for $l \ge 1$ the CG wave equation yields for the corresponding eigenvalues of a one-electron system those of the Klein-Gordon (KG) equation (Gordon 1926, Klein 1927), which is however only appropriate for spin-zero particles. In order to obtain the exact eigenvalues of the Dirac equation (Dirac 1928a,b, 1929) for spin-half particles like an electron one has to keep the Darwin term, although its contributions are small for $l \ge 1$. Second, the neglect of the spin-orbit term does neither lead to properly averaged eigenvalues nor eigenfunctions for $l \ge 1$. This is quite obvious from the energy dependency of the quasirelativistic operators: although the averaging yields $\kappa = -1$ for the relativistic quantum number κ and suggests a neglect of the spin-orbit term, it should be noted that all three quasirelativistic operators still depend on the one-particle energy ε_A , which is different for the two cases $j = l \pm \frac{1}{2}$. A properly averaged quasirelativistic Hamiltonian should be set up according to

$$\mathcal{H}_{\rm WB} = \mathcal{H}_{\rm S} + \frac{1}{2l+1} (l\mathcal{H}_{-} + (l+1)\mathcal{H}_{+}), \tag{40}$$

with

$$\mathcal{H}_{\pm} = \mathcal{H}_{\mathrm{MV},\pm} + \mathcal{H}_{\mathrm{D},\pm} + \mathcal{H}_{\mathrm{SO},\pm} \qquad \left(\pm \text{ for } j = l \pm \frac{1}{2}\right). \tag{41}$$

Unfortunately, neither the one-particle energies nor the local potential used in the quasirelativistic operators are known. For the local potentials V_{\pm} one may use an average potential, whereas estimates for the one-particle energies ε_{\pm} may be obtained by first-order perturbation theory in every SCF iteration.

The results of calculations within the WB or CG scheme for valence properties of atoms are usually in rather good agreement with the more accurate DHF results (Kobus and Jaskólski 1987). The WB method has been implemented into a standard nonrelativistic atomic structure program and is used by the Stuttgart group to generate quasirelativistic pseudopotentials (Dolg et al. 1989b, Küchle et al. 1991). An alternative quasirelativistic method was developed by Barthelat et al. (1980) and is used to generate reference data for the pseudopotentials developed in the Toulouse group. A discussion of quasirelativistic methods for atoms may be found in an article by Karwowski and Kobus (1985). The WB scheme was also applied in molecular quasirelativistic one-component multiple-scattering X_{α} calculations on UF₆ and UO₂²⁺ (Boring and Wood 1979a,b).

2.1.4. Density-functional methods

For heavy-element compounds like lanthanide-containing molecules correlation effects are as important as relativistic effects when an accurate description of the system is desired. Instead of using the 'traditional' wavefunction-based methods, e.g. the Dirac– Hartree–Fock approach for the creation of a one-particle basis and the subsequent systematic improvement of the solution within this basis by a configuration interaction scheme, one might also consider to apply density-functional theory (DFT) as an alternative approach to solve the many-electron problem (Hohenberg and Kohn 1964, Kohn and Sham 1965). Relativistic extensions of DFT have been formulated (Ramana and Rajagopal 1983); the existing computational schemes may be regarded as approximations.

The Dirac-Hartree-Fock-Slater discrete-variational (DHFS-DV) (Rosén and Ellis 1975) and multiple-scattering (DHFS-MS) or scattered-wave (DHFS-SW) (Case 1982, Yang 1983) methods solve four-component equations based on the one-particle Dirac Hamiltonian similar to the nonrelativistic Kohn-Sham equations, and have been applied to lanthanide containing systems, e.g. for the interpretation of photoelectron spectra of lanthanide trihalides (Ruščić et al. 1983). Corresponding quasirelativistic one- and twocomponent schemes, using besides the nonrelativistic kinetic energy operator a massvelocity, Darwin and spin-orbit term, have also been developed, e.g. the quasirelativistic X_{α} scattered wave method (Thornton et al. 1980). The Amsterdam group developed a quasirelativistic Hartree-Fock-Slater method based on self-consistent perturbation theory (Snijders and Baerends 1978, Snijders et al. 1979). Recently the method has been applied to calculate the electronic structure of selected lanthanide diatomics and to investigate the lanthanide contraction (Wang and Schwarz 1995, Wang et al. 1995). Gradient-corrected exchange (Becke 1988) and self-interaction-corrected (Stoll et al. 1978, 1980) correlation (Vosko et al. 1980) energy functionals were found to work satisfactorily for the outer valence shells, but less well for the localized lanthanide 4f shells. A scalar relativistic extension of the linear combination of Gaussian type orbitals local density-functional (LCGTO-LDF) (Dunlap and Rösch 1990) method based on the Douglas-Kroll transformation (Douglas and Kroll 1974) has recently been presented and implemented (Rösch and Häberlen 1992, Häberlen and Rösch 1992). Currently one application of this method to a lanthanide containing system has been published, i.e. Ce @ C₂₈ (Rösch et al. 1993).

Many of the early, rigorous investigations of lanthanide-containing molecules have been performed with density-functional methods. They are especially useful for the investigation of photoelectron spectra, however they are certainly not the method of choice when one is interested, e.g., in the energy differences between electronic states arising from an open f shell, especially when configurations with different 4f occupation numbers are involved.

2.2. Valence-electron methods

The idea behind any valence-electron (VE) method is clearly chemical: as is evident from the similarities between elements of a group in the Periodic Table only the valence electrons are responsible for the chemical behavior of an atom. Of course, in quantum mechanics it is not possible to separate a system of indistinguishable particles like electrons into two sets without further approximation, e.g. the core-valence separation results in the neglect of core-valence correlation. However, when we stay in the framework of one-particle models like the Hartree-Fock or Dirac-Hartree-Fock approach we certainly may distinguish between core and valence orbitals. It is at this level of theory that pseudopotential (PP), effective core potential (ECP) or model potential (MP) methods are most easily introduced. Usually the core orbitals are assumed to be transferable for atom and molecules regardless of the electronic state, i.e. the frozen-orbital or frozencore approximation is another basic assumption of valence-only approaches. A further more drastic approximation seems to be the actual replacement of the core electron system via the introduction of a PP. ECP or MP. The advantage of these approximate ab initio methods is not only the considerable reduction of computational effort due to the restriction to a valence electron system, but also the possibility to easily take into account the major relativistic effects. Formally, in the calculations only a nonrelativistic valence model Hamiltonian is applied, however it is hoped that the major relativistic contributions enter into the calculation via a corresponding adjustment of the free parameters in the potentials. If we abandon solving the Schrödinger equation for a given model Hamiltonian as exactly as possible but rather parametrize the elements of a corresponding Fock matrix, we come to semiempirical methods like the intermediate neglect of differential overlap or the extended Hückel approach discussed here. Besides relativistic effects the parametrization may now also account for correlation contributions which are rather difficult to calculate in practice with ab initio schemes.

2.2.1. Pseudopotentials, effective core potentials and model potentials

By means of the introduction of pseudopotentials the many-electron system is divided in a core-electron system implicitly included by the pseudopotentials and a valenceelectron system explicitly treated in the quantum-chemical calculations. The all-electron Hamiltonian is replaced by the following valence-only model Hamiltonian for n_v valence electrons:

$$\mathcal{H}_{v} = \sum_{i}^{n_{v}} h_{v}(i) + \sum_{i < j}^{n_{v}} g_{v}(i, j) + V_{cc}.$$
(42)

As for the all-electron case, nonrelativistic, quasirelativistic or relativistic formulations are also possible in pseudopotential calculations for the one- and two-electron valence-only operators h_v and g_v , respectively. The mutual Coulomb interaction between the nuclei has been replaced by the core-core interaction potential V_{cc} .

Early work based on a statistical treatment of the core electrons was published by Hellmann (1935) and Gombás (1935) for molecular and solid-state physics, respectively. Quantum-mechanical justifications in the framework of the Hartree and Hartree–Fock theories were given by Fényes (1943) and Szépfalusy (1955, 1956), respectively. The first derivation of the pseudopotential approach within the Hartree–Fock formalism which came to general attention is due to Phillips and Kleinman (1959) and was later generalized by Hazi and Rice (1968). The accuracy and limitations of the pseudopotential approach

have been discussed by Schwarz (1968) and T.-C. Chang et al. (1977). Relativistic derivations of pseudopotential approaches can be formulated in principle (Kleinman 1980). It should be noted that upon the introduction of a pseudopotential from such a purely theoretical point of view the form of the valence-only operators h_v and g_v has to be altered in a rather complicated way with respect to the corresponding all-electron operators h and g. However, for practical purposes requiring a certain degree of accuracy it is desirable to go to a valence-only Hamiltonian as simple as possible. It was long intrigued if valence electrons in atoms and molecules behave relativistically (Rose et al. 1978) or not (Datta et al. 1978), however it is a widely accepted fact today that for not too highly charged cores the valence-electron system can be treated in a formally nonrelativistic scheme, i.e., the relativistic Dirac one-particle operator is replaced by the corresponding nonrelativistic expression and all relativistic effects are put into the pseudopotential V_{cv} by means of a suitable parametrization, i.e.

$$h_{\rm v}(i) = -\frac{1}{2}\Delta_i + V_{\rm cv}.$$
(43)

Both steps, introduction of the pseudopotential and simplification of the Hamiltonian, may formally be carried out in any order, resulting in different expressions for the valenceonly Hamiltonian (Hafner and Schwarz 1979, Pyper 1980a,b, 1981, Pyper and Marketos 1981). The derivation of pseudopotentials to be used within the Dirac-Hartree–Fock scheme has also been attempted (Ishikawa and Malli 1981, 1983, Dolg 1995). We note that the derivation of valence-only Hamiltonians used in pseudopotential theory is neither unique nor may be carried out without a multitude of approximations. Therefore, in practice a proper adjustment of free parameters in a suitably chosen model Hamiltonian seems to be much more important than a lengthy theoretical derivation.

The traditional and most widely applied approach uses pseudopotentials adjusted in atomic calculations for specific chemical elements, which are usually superimposed in the subsequent molecular calculations to give an approximate molecular pseudopotential V_{cv} , i.e.

$$V_{\rm cv} = \sum_{i}^{n_{\rm v}} \sum_{\lambda}^{N} \left(-\frac{Q_{\lambda}}{r_{\lambda i}} + \Delta V_{\rm cv}^{\lambda}(\boldsymbol{r}_{\lambda i}) \right) + \cdots$$
(44)

The leading point-charge terms usually have to be augmented by correction terms ΔV_{cv}^{λ} , which may be formulated in a local, semilocal or nonlocal form. The advantage of these element-specific pseudopotentials is their economy regarding the number of necessary parameter sets to cover the whole Periodic Table. Once they have been generated for every element separately, they may be applied in calculations on compounds with arbitrary composition. Moreover, the pseudopotential adjustment itself is further simplified when the central-field approximation is used in the necessary atomic calculations.

Besides these pseudopotentials for chemical elements there have been several approaches to replace groups of atoms, e.g. functional groups or polyatomic ligands, by a pseudopotential (Ohta et al. 1983, Von Arnim 1993, Von Arnim and Peyerimhoff 1993).

Such group or fragment pseudopotentials require higher effort during the adjustment, but may be rewarding when larger systems are to be treated. We will not discuss this topic here.

For the mutual repulsion of the nuclei represented by V_{cc} the point charge model gives the leading terms, which often yield a sufficiently accurate description. However, in some cases the use of large and diffuse cores makes it necessary to add corrections to the point charge repulsion between the cores due to their mutual penetration, i.e.

$$V_{\rm cc} = \sum_{\lambda < \mu}^{N} \left(\frac{Q_{\lambda} Q_{\mu}}{r_{\lambda \mu}} + \Delta V_{\rm cc}^{\lambda \mu}(r_{\lambda \mu}) \right) + \cdots$$
(45)

The corresponding corrections have to be derived from molecular calculations for every pair of elements occurring in the compounds to be investigated. At the cost of a higher number of parameter sets, significant computational savings result from the use of the larger pseudopotential cores, however the accuracy may be somewhat lower.

One may distinguish methods that try to retain the radial nodes in the valence orbitals when removing the core-electron system and use projection operators based on core orbitals or spinors (core projection model, T.-C. Chang et al. 1974, nonlocal potentials), and those that formally apply a transformation to derive (for the energetically lowest subshell of each symmetry which is kept in the valence) nodeless pseudo-orbitals from the corresponding all-electron valence orbitals and use projection operators based on spherical harmonics or spinor spherical harmonics (angular projection model, T.-C. Chang et al. 1974, semilocal potentials). Local potentials, i.e. forms without projection operators which have been used in early applications (Preuß 1955), proved to be too inaccurate. We will briefly review only work for the angular projection scheme, since to our knowledge the core projection method has not been applied for the lanthanides yet. For details of this approach we refer to the original papers summarized briefly in the following. Sakai et al. (1987a,b) have published two sets of nonrelativistic and quasirelativistic model potentials for the transition metals ${}_{21}Sc - {}_{30}Zn$ and ${}_{39}Y - {}_{80}Hg$, respectively. The relativistic extension of the nonrelativistic method of Bonifacic and Huzinaga (1974) which was later improved by Sakai and Huzinaga (1982) is due to Klobukowski (1983). The necessary reference data are obtained from quasirelativistic atomic Cowan-Griffin calculations. The ab initio model potential method (AIMP) (Huzinaga et al. 1987, Seijo et al. 1989) and the quasirelativistic Cowan-Griffin based extension (CG-AIMP) (Barandiarán et al. 1990, Barandiarán and Seijo 1992) has been developed for main group and transitions elements and proved to be reliable (e.g. Barandiarán and Seijo 1994).

Most of the modern pseudopotentials or effective-core potentials use a semilocal ansatz for at least those angular quantum numbers of the occupied one-electron states present in the core and the valence. For the higher angular quantum numbers some approaches keep a local potential, some others do not. For two-component calculations the following ansatz can be used:

$$\Delta V_{\rm cv}^{\lambda}(\boldsymbol{r}_{\lambda i}) = \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} \left(V_{lj}^{\lambda}(\boldsymbol{r}_{\lambda i}) - V_{L}^{\lambda}(\boldsymbol{r}_{\lambda i}) \right) P_{lj}^{\lambda} + V_{L}^{\lambda}(\boldsymbol{r}_{\lambda i})$$
(46)

with the projection operator onto spinor spherical harmonics

$$P_{lj}^{\lambda} = P_{l,\,l\pm 1/2}^{\lambda} = \sum_{m_j=-j}^{J} |ljm_j\rangle \langle ljm_j|.$$

$$\tag{47}$$

After averaging over spin-orbit interaction the following form for one-component, i.e. scalar relativistic, calculations is obtained:

$$\Delta V_{\rm cv,av}^{\lambda}(\boldsymbol{r}_{\lambda i}) = \sum_{l=0}^{L-1} \left(V_l^{\lambda}(\boldsymbol{r}_{\lambda i}) - V_L^{\lambda}(\boldsymbol{r}_{\lambda i}) \right) P_l^{\lambda} + V_L^{\lambda}(\boldsymbol{r}_{\lambda i}).$$
(48)

with the projection operator onto spherical harmonics

$$P_l^{\lambda} = \sum_{m_l=-l}^{l} |lm_l\rangle \langle lm_l|.$$
⁽⁴⁹⁾

Pseudopotentials of this type require only an extension of the one-electron integral routines and therefore may be used in any standard quantum-chemistry code to perform calculations in which the major scalar relativistic effects are included.

The corresponding spin-orbit operator can be written as

$$\Delta V_{\rm cv,so}^{\lambda}(\mathbf{r}_{\lambda i}) = \sum_{l=1}^{L} \frac{\Delta V_{l}^{\lambda}}{2l+1} \left[l P_{l,l+1/2}^{\lambda} - (l+1) P_{l,l-1/2}^{\lambda} \right]$$
(50)

with the difference of the radial quasirelativistic potentials

$$\Delta V_l^{\lambda}(r_{\lambda i}) = V_{l,l+1/2}^{\lambda}(r_{\lambda i}) - V_{l,l-1/2}^{\lambda}(r_{\lambda i}).$$
⁽⁵¹⁾

Hafner and Schwarz (1979) as well as Pitzer and Winter (1988) suggested a form of the spin-orbit operator which is more convenient to use in molecular calculations when symmetry can be exploited:

$$\Delta V_{\rm cv,so}^{\lambda}(\boldsymbol{r}_{\lambda l}) = \sum_{l=1}^{L} \frac{2\Delta V_{l}^{\lambda}(\boldsymbol{r}_{\lambda l})}{2l+1} P_{l}^{\lambda} \boldsymbol{l} \boldsymbol{s} P_{l}^{\lambda}.$$
(52)

The proper adjustment of accurate pseudopotentials is mainly a matter of experience, and the development of the modern methods used today evolved from many important, more or less successful attempts made since the introduction of pseudopotentials into quantum chemistry about 60 years ago (Hellmann 1935, Gombás 1935). However, although many findings of these older investigations have been incorporated into the state-of-the-art methods, most of these approaches themselves are only of historical interest and will not be reviewed here. A deeper discussion of some of these methods, including many references to the original papers may be found in various older review articles, e.g. by Weeks, Hazi and Rice (1969), Bardsley (1974), Dixon and Robertson (1978), or Szasz (1985). More recent work was reported by Hay (1983), Pitzer (1983, 1984), Kahn (1984), Krauss and Stevens (1984), Christiansen et al. (1985), and Gropen (1988).

Essentially two lines are followed for the derivation of pseudopotentials or effectivecore potentials creating nodeless pseudo-orbitals. One approach uses as reference data the shape of the valence orbitals or spinors in the spatial valence region and their corresponding one-particle energies. In the spatial core region the one-particle functions are smoothed according to special prescriptions and the radial Fock equation is solved for the potential, which is then usually fitted by linear combinations of Gaussians times powers of r.

The Toulouse quantum-chemistry group created quasirelativistic pseudopotentials based on the atomic structure method developed by Barthelat et al. (1980) and the general procedure of adjustment devised by Durand and Barthelat (1974, 1975). The pseudopotential is constructed in such a way that the pseudo-orbitals coincide best with the all-electron valence orbitals and are smooth in the core region, i.e. an approach which has later been termed 'norm-conserving' (Hamann et al. 1979) or 'shape-consistent' (Christiansen et al. 1979, Rappé et al. 1981). No parameter sets for the lanthanides and actinides have been published up to now.

Bachelet et al. (1982) generated norm-conserving one- and two-component quasirelativistic pseudopotentials for density-functional calculations for $_1$ H through $_{94}$ Pu according to the prescription given by Bachelet and Schlüter (1982). A molecular application for La@C₈₂ will be discussed later.

Wadt and Hay (1985) have published one-component quasirelativistic effective core potentials for the main group elements $_{11}$ Na $_{83}$ Bi. Two sets of parameters were presented for the d transition metals $_{21}$ Sc $_{80}$ Hg with large (Hay and Wadt 1985a) and small (Hay and Wadt 1985b) cores. A parametrization for alkaline elements $_{19}$ K $_{-55}$ Cs and alkaline earth elements $_{20}$ Ca $_{-56}$ Ba using small cores has also been derived (Hay and Wadt 1985b). The method of derivation is the shape-consistent extension of the previous nonrelativistic prescription by Kahn, Baybutt and Truhlar (1976) and the corresponding quasirelativistic scheme by Kahn, Hay and Cowan (1978) based on the Cowan–Griffin atomic structure approach (Cowan and Griffin 1976). An approximate method to include spin–orbit coupling was presented by Wadt (1982). Except for $_{57}$ La no parameter sets are available for the lanthanide elements.

Pitzer, Christiansen and coworkers have generated shape-consistent one- and twocomponent quasirelativistic effective core potentials starting from all-electron DHF calculations (Christiansen et al. 1979) for the elements $_{3}Li_{-94}Pu$, i.e. $_{3}Li_{-18}Ar$ (Pacios and Christiansen 1985), $_{19}K_{-36}Kr$ (Hurley et al. 1986), $_{37}Rb_{-54}Xe$ (LaJohn et al. 1987), $_{55}Cs_{-57}La$ and $_{72}Hf_{-86}Rn$ (Ross et al. 1990). Recently parameters sets for the lanthanide series $_{58}Ce_{-71}Lu$ (Ross et al. 1994) and the lighter actinide elements $_{89}Ac_{-94}Pu$ (Ermler et al. 1991) have been presented. The relativistic formulation, although for non-shapeconsistent Phillips-Kleinman pseudopotentials, has been presented by Lee et al. (1977). Core-valence correlation effects can also be included (Christiansen 1986).

Stevens and coworkers have published shape-consistent one-component quasirelativistic pseudopotentials, i.e. ${}_{3}\text{Li}-{}_{18}\text{Ar}$ (Stevens et al. 1984), ${}_{19}\text{K}-{}_{57}\text{La}$ and ${}_{72}\text{Hf}-{}_{86}\text{Rn}$ (Stevens et al. 1992). Cundari and Stevens (1993) presented the corresponding parameters for the lanthanides ${}_{58}\text{Ce}-{}_{71}\text{Lu}$. Spin-orbit potentials have not been published but may be derived (Stevens and Krauss 1982) since the reference data are taken from all-electron DHF calculations.

The other approach does not rely on quantities like orbitals and orbital energies only defined in effective one-particle models, but rather on quantum-chemical observables like total valence energies. The pseudopotential parameters are derived in atomic calculations by a least-squares fit to valence energies of electronic states lying in the spectral region of interest for the atoms and its ions. Such energy-adjusted ab initio pseudopotentials and corresponding optimized valence basis sets are available for almost the entire Periodic Table from the Stuttgart group, i.e., the main group elements of groups 13-17 (Bergner et al. 1993), ₈₀Hg-₈₆Rn (Küchle et al. 1991), the d transition metals ₂₁Sc-₃₀Zn (Dolg et al. 1987), ₃₉Y-₈₀Hg (Andrae et al. 1990), ₁₀₅Ha (Dolg et al. 1993b), ₁₁₁E and ₁₁₂E (Seth et al. 1995). Complete sets for the lanthanides ${}_{57}La - {}_{71}Lu$ (Dolg et al. 1989a,b, 1991d, 1993a), and actinides $_{89}Ac_{-103}Lr$ (Küchle et al. 1994) are also available. For most elements also nonrelativistic parametrizations exist, which are useful for the accurate determination of relativistic effects in molecules. The two sets published for the lanthanides treat the 4f shell either as part of the core space or explicitly in the valence space. The first set allows calculations within the superconfiguration model advocated by Field (1982) and may be combined with ligand field theory to obtain information on the individual states of a superconfiguration (Dolg et al. 1993a). The Stuttgart group also published accurate semiempirical pseudopotentials which account for core-valence correlation effects by means of core-polarization potentials for most of the main group elements, i.e. the alkaline and alkaline earth atoms (Fuentealba et al. 1982, 1985, 1987) and for groups 13-17 with $n \leq 5$ (Igel-Mann et al. 1988).

Whenever one wishes to investigate spectroscopic properties of lanthanide compounds one needs to include spin-orbit coupling in the calculations. Whereas for the AE DHF or DHFR calculations and subsequent CI treatments it is necessary to work respectively in jj and $\omega\omega$ coupling for atoms and molecules, one has essentially three different choices at what stage of a PP calculation spin-orbit interaction is accounted for.

The first and most efficient approach is to account only for scalar relativistic effects during the SCF and CI steps, i.e. to work exclusively in LS and $\Lambda\Sigma$ coupling for atoms and molecules, respectively. All steps of the calculation may be performed with standard ab initio codes and only real integrals, matrix elements and wavefunctions are involved. The correlated many-electron wavefunctions of the LS or $\Lambda\Sigma$ states coupled by the spinorbit terms in the Hamiltonian are then used to build a usually small Hamiltonian matrix which includes spin-orbit matrix elements. The diagonalisation of this generally complex matrix yields the desired total energies and wavefunctions in an intermediate coupling scheme. The method directly gives insight how much the LS or $\Lambda\Sigma$ states contribute to the states of interest. A computational scheme of this type developed by the Toulouse group is the CIPSO (CIPSI adapted for spin-orbit interaction) algorithm (Teichteil et al. 1983), which may be viewed as an extension of the original two-class CIPSI (configuration interaction by perturbative selection of the zeroth-order interacting space) method (Huron et al. 1973). The CIPSO algorithm has been successfully applied to CeO (Dolg et al. 1991a) and YbO (Dolg et al. 1992c).

A second approach stays in LS or $\Lambda\Sigma$ coupling during the SCF step, but accounts for spin-orbit interaction together with electron correlation in the CI step. The Hamiltonian matrix is complex and usually built in the basis of determinants or double group adapted linear combinations. Programs that work according to this strategy have been written by Christiansen et al. (1982) and A.H.H. Chang and Pitzer (1989). The latter code exploits the fact that for some cases (e.g. D_{2h}^* or C_{2v}^*) a complex arithmetic may be avoided since the matrix elements of a row or column are either purely real or purely imaginary (Pitzer and Winter 1988). It has been used in several applications for lanthanide (e.g. Dolg et al. 1995) and actinide (e.g. A.H.H. Chang et al. 1994) compounds. It is also part of the INDO/S-CI programs developed by Rösch, Zerner and coworkers (Kotzian et al. 1989a).

The third method includes spin-orbit interaction already at the SCF level, i.e. as in the AE DHF or DHFR method one has to work in the jj and $\omega\omega$ coupling scheme for atoms and molecules, respectively. In contrast to the other two approaches one has to deal with complex integrals and wavefunctions already at the SCF level. In addition to the double point group symmetry the Kramers degeneracy of the spinors may be exploited to reduce the computational effort. SCF and MRCI programs falling into this category have been written by the group in Siegen (Hafner and Schwarz 1979, Esser et al. 1981, Esser 1983, 1984a,b). A MCSCF program for linear molecules was presented by Christiansen and Pitzer (1980). More recently a SCF program was described by Lee and Lee (1992).

2.2.2. Intermediate neglect of differential overlap method

Ab initio all-electron or valence-electron calculations face the problem that for accurate electronic structure calculations of lanthanide compounds large one-electron basis sets and long configuration interaction expansions are required. In most cases, especially when electronic states with leading configurations that formally correspond to differing 4f occupations are considered, several g functions have to be included to correlate the 4f shell. Moreover, since the 4f shell of the lanthanide atom is rather compact with a maximum electron density at a smaller radial distance from the nucleus than the one of the fully occupied 5s and 5p shells, it is not reasonable to freeze the latter orbitals in the correlation treatment, e.g. at least 12 and 24 electrons have to be correlated for Ce $(4f^{1}5s^{2}5p^{6}5d^{1}6s^{2})$ and Yb $(4f^{14}5s^{2}5p^{6}6s^{2})$, respectively. The resulting high numbers of valence electrons quickly lead to unmanageable configuration interaction expansions. In addition, size-consistency problems arise due to the increasing number of electrons. Finally, for open 4f shells spin–orbit interaction should be included in the calculations, however the ab initio methods at hand which simultaneously treat electron correlation and spin–orbit interaction are computationally rather demanding.

In view of the briefly outlined problems of ab initio approaches semiempirical schemes appear to be very attractive. An early intermediate neglect of differential overlap (INDO) (Pople et al. 1967, Pople and Beveridge 1970) study on the bis(cyclooctatetraene)cerium(III) anion was performed by Clack and Warren (1976). Formulae for the complete/intermediate neglect of differential overlap (CNDO/INDO) formalism for f block elements have been published by Fanning and Fitzpatrick (1980). An unrestricted INDO program was written by the Peking group (Ren et al. 1982, Li et al. 1983) and applied to several organo-lanthanide complexes, e.g. $bis(n^5$ cyclopentadienyl)ytterbium(III) methyl (Xu and Ren 1986). In recent years Rösch, Zerner and coworkers developed an intermediate neglect of differential overlap method with separate parametrizations for ground state (INDO/1) (Culberson et al. 1987) and spectroscopic (INDO/S-CI) (Kotzian et al. 1992) investigations of lanthanide compounds. Whereas the INDO/1 approach is used for the derivation of molecular geometries using gradient methods for a single state within the UHF or RHF formalism or for an average of states using a corresponding definition of the Fock matrix, the INDO/S-CI allows the calculations of term energies for excited states including the effects of spin-orbit interaction. The ground-state version is characterized by Slater-type orbital basis sets derived from atomic Dirac-Hartree-Fock calculations, effective one-electron one-center core integrals estimated from experimental ionization potentials, the inclusion of all one- and two-center two-electron integrals as well as parameter sets for effective oneelectron two-center integrals based on the molecular geometries of CeCl₃ and LuCl₃. In the spectroscopic variant the one-center two-electron integrals are derived from experimental ionization potentials and electron affinities. The two-center two-electron integrals are calculated from the corresponding one-center integrals using a distancedependent formula. The spin-orbit term in the Hamiltonian is restricted to include the dominant one-center contributions, the necessary parameters for the 4f shell have been taken from atomic spectroscopy, whereas those for the 5d and 6p orbitals were derived from the spectrum of LaO, LuO and LuF. For the spin-orbit CI either the double group CI program originally developed by Pitzer (A.H.H. Chang and Pitzer 1989, Kotzian et al. 1989a) or a CI technique based on Rumer spin functions (Kotzian et al. 1991) is applied. Typically the CI expansions only account for single excitations from a set of reference configurations describing the electronic states of interest. The molecular orbitals are taken from spin-orbit averaged SCF calculations with a Fock operator describing a configurational average. For more details of the INDO methods we refer the reader to the original papers. Both the INDO/1 and the INDO/S-CI methods have been successfully applied to several lanthanide systems, some of which currently cannot be investigated by ab initio approaches, e.g. the para-dimetallated σ -phenylene complexes $[(cp_{M})_{2}C_{6}H_{4}]$ (M=Sc, Lu) (Jahns et al. 1992) or the hydrated cerium(III) model complexes $[Ce(H_2O)_n]^{3+}$ (n=8,9) (Kotzian and Rösch 1992). Recently the INDO/1 model has also been extended to the actinide elements (Cory et al. 1994), however the first results for several tetrahalides MX_4 and hexahalides MX_6 (M=Ac, Th, Pa, U, Np, Pu; X = F, Cl seem to be less encouraging than those obtained previously for the lanthanides. The main difficulty encountered for semiempirical methods like INDO in the actinide series probably is the lack of sufficient and accurate reference data, especially for the transuranium elements.

2.2.3. Extended Hückel method

One of the simplest methods of relativistic quantum chemistry is the extension of the extended Hückel molecular orbital theory (EHT) (Hoffmann and Lipscomb 1962a,b, Hoffmann 1963, Lohr and Lipscomb 1963) to include spin-orbit effects (REX) by Lohr and Pyykkö (1979). The method has been reviewed by Pyykkö (1988b). It may be viewed as a convenient and very inexpensive procedure for a systematic 'extrapolation' of the results of atomic Dirac-Hartree-Fock and Hartree-Fock calculations to molecules in order to get insight into relativistic effects on chemical bonding. A computer program with both a relativistic and a nonrelativistic parametrization has been improved several times since the original proposal of the method and is generally available (Pyykkö 1988b).

In the extended Hückel type approaches one seeks a solution of the following eigenvalue problem of an unspecified effective one-electron Hamiltonian

$$(H - \varepsilon S) c = 0. \tag{53}$$

A basic assumption is that the matrix elements H_{ij} of the Hamiltonian are related to the corresponding overlap matrix elements S_{ij} , i.e.

$$H_{ij} = f(H_{ii}, H_{jj}) S_{ij} \quad \text{with} \quad f(H_{ii}, H_{jj}) = k(H_{ii} + H_{jj})/2.$$
(54)

The proportionality constant k is usually assigned a value of approximately 1.75. The overlap matrix elements S_{ij} are calculated with respect to a set of two component basis functions with $|lsjm\rangle$ quantization. The radial parts were chosen to be one or two Slater functions yielding $\langle r^k \rangle$ (k=-1, 0, 1, 2) expectation values as close as possible (Lohr and Jia 1986) to the Dirac–Hartree–Fock or Hartree–Fock results tabulated by Desclaux (1973) for the relativistic and nonrelativistic case, respectively. The diagonal Hamiltonian matrix elements H_{ii} were set equal to the corresponding orbital energies from Desclaux's tables. Due to the use of a two-component $|lsjm\rangle$ basis set the matrices H and S are generally complex and of dimension $2n \times 2n$, when n is the number of spatial orbitals.

The current program version (Pyykkö 1988b) was speeded up by Rösch through the use of quaternionic algebra (Rösch 1983) and also allows for charge iteration (Larsson and Pyykkö 1986). A corresponding band-structure version also exists (Lohr 1987). Numerous results have been published since the introduction of the method, e.g. on all 60 trihalides of the lanthanides (Pyykkö and Lohr 1981, Lohr and Jia 1986).

2.2.4. Ligand field theory, angular overlap model and other methods

There are a number of computational schemes that have been applied frequently for lanthanide systems but will not be reviewed here in more detail. Ligand field theory (LFT) has proven to be a very useful tool to interpret the sometimes extremely complex spectra of lanthanide systems (Field 1982, Dulick 1982, McDonald 1985). An alternative

approach that takes into account covalent contributions is the angular overlap model (AOM) (Jørgensen et al. 1963, Schäffer and Jørgensen 1965, Urland 1976).

A so-called 'sparkle model' for europium(III) in the semiempirical Austin Model 1 (AM1) (Dewar et al. 1985) scheme was recently proposed (Andrade et al. 1994, 1995). Essentially the lanthanide ion is treated as a positive point charge together with a suitable repulsive potential to model core-valence interaction.

Models based on the electric multipole expansion have been used to explain structures, force constants and binding energies of lanthanide compounds (Guido and Gigli 1974, Ackermann et al. 1976, Myers 1976, Jia and Zhang 1988).

3. Results

3.1. Atoms

Many results for relativistic atomic calculations on lanthanide elements are available in the literature. Most of these studies use the finite difference single- or multiconfiguration Dirac-Hartree-Fock (DHF or MCDHF) approach based on the Dirac-Coulomb Hamiltonian. Some of them also include the Breit or Gaunt interaction. It is beyond the scope of this review to summarize these studies. However, we want to mention as an example recent results for Pr³⁺ (Eliav et al. 1995) which in our opinion have a higher quality than previous studies and give a promising perspective for future investigations on lanthanide atoms and ions; these are relativistic coupled-cluster singles and doubles (CCSD) calculations based on the Dirac-Coulomb(-Breit) Hamiltonian (Eliav et al. 1994a). These studies use large one-particle basis sets with up to i functions and reproduce the experimental excitation energies of $Pr^{3+} 4f^2$ with an average error of only 222 cm⁻¹. We summarize some of these results in table 10 and compare them to the best available optimized-level MCDHF calculations by Cai et al. (1992) which include several hundreds of relativistic configurations for each J level. For comparison 'uncorrelated' averagelevel (AL) MCDHF calculations have been performed by the authors. The spin-orbit splittings of the LS terms are well reproduced even by the MCDHF AL calculations (cf. the ³H state), however the importance of electron correlation effects for the accurate calculation of the splittings between the LS terms is obvious from the data listed in table 10.

Things become more difficult when energy differences between states arising from configurations with different 4f occupation numbers are considered. An example are the $4f^{14}6s^1$ and $4f^{13}6s^2$ configurations of Yb⁺ and the $4f^{14}$ and $4f^{13}6s^1$ configurations of Yb⁺⁺. It has been derived from ligand field theory (LFT) that the lowest states of the latter two configurations are separated by less than 1000 cm^{-1} in YbO, which may be approximated as a Yb²⁺O²⁻ ion pair (McDonald et al. 1990). Before the treatment of the molecule (Dolg et al. 1992c) is attempted it is of interest how well ab-initio-based methods can perform for atoms or ions in such cases. The corresponding molecular results are discussed later. The results of uncorrelated and correlated atomic calculations are

Level		Theoretical values ^a		Experimental
	MCDHF, AL ^b	MCDHF, OL ^c	CCSD ^d	values ^e
³ H ₄	0	0	0	0
³ H ₅	2205	2337	2270	2152
³ H ₆	4547	4733	4635	4389
³ F ₂	6767	4984	4843	4997
³ F ₃	8169	6517	6354	6415
³ F ₄	8157	6950	6843	6855
${}^{1}G_{4}$	11146	10207	10001	9921
¹ D ₂	23416	18153	16998	17334
³ P ₀	29426	22776	21155	21390
³ P ₁	29982	23450	21791	22007
¹ I ₆	28041	25854	22010	22212
³ P ₂	31084	24653	23051	23161
¹ S ₀	64619	50517	49194	50090
Avg. error	4720	853	222	

Table 10 Term energies (cm⁻¹) of levels of Pr^{3+} 4f² from various calculations and from experiment

^a All theoretical results refer to a Dirac-Coulomb Hamiltonian.

^b Average-level (AL) multi-configuration Dirac-Hartree-Fock (MCDHF) calculations corresponding to one nonrelativistic configuration (Dolg 1995). Only 4f² was considered.

^c Large scale optimized-level (OL) calculations corresponding to 39 nonrelativistic configurations (Cai et al. 1992). 38 replacements into spinors of up to k symmetry from $4f^2$ were considered, leading to 354, 858, 1386, 1579, 1708, 1535 and 1344 relativistic configurations for J=0 to J=6.

^d Singles and doubles coupled-cluster (CCSD) calculations (Eliav et al. 1995). Kinetically balanced (29s23p19d14f10g6h4i) basis set; the n=4 and n=5 shells were correlated.

^e Martin et al. (1978).

summarized in tables 11 and 12, respectively. Spin-orbit splittings are listed in table 13. The $4f^{14}6s^{12}S \rightarrow 4f^{13}6s^{22}F$ excitation energy of Yb⁺ has contributions of -6.45 eV and 3.28 eV from relativity (HF vs. DHF) and electron correlation (DHF vs. exp.), respectively. The corresponding values for the $4f^{14}$ is $\rightarrow 4f^{13}6s^{11,3}F$ energy separation are -6.44 eV and 3.75 eV, respectively. The spin-orbit averaged experimental excitation energies are 3.20 eV and 4.86 eV. Large-scale multi-reference configuration interaction (MRCI) calculations using a quasirelativistic pseudopotential (PP) yield values of 3.25 eV and 5.08 eV in rather good agreement with the experimental values. (Here and in the following we will cite CI results that have been corrected for size-consistency errors using the formula given e.g. by Langhoff and Davidson 1974 whenever these are available.) The corresponding values obtained with the coupled-pair functional (CPF) approach are 3.21 eV and 4.91 eV. It should be noted however, that these apparently good results are due to several errors at different stages of the calculations, i.e. errors in the reference data used for the PP adjustment (0.18 eV and 0.18 eV), errors due to the PP itself (0.11 eV and 0.21 eV). The

ELECTRONIC STRUCTURE CALCULATIONS

Atom/ion	Configuration	LS		AE re		PP results °		
			HF	DHF	+QED	WB	a	b
Yb	$4f^{14} 6s^2$	¹ S	0.00	0.00	0.00	0.00	0.00	0.00
Yb+	$4f^{14} 6s^{1}$	${}^{2}\mathbf{S}$	4.78	5.15	5.15	5.14	5.06	5.06
	4f ¹³ 6s ²	² F	11.15	5.07	5.19	5.24	5.27	5.38
Yb++	4f ¹⁴	^{1}S	15.30	16.44	16.43	16.42	16.18	16.16
	4f ¹³ 6s ¹	³ F	22.83			17.68	17.56	17.73
				17.55	17.66			
	4f ¹³ 6s ¹	۱F	22.91			17.78	17.65	17.83

Table 11 Ionization energies from uncorrelated quasirelativistic pseudopotential calculations in comparison with allelectron results^a

^a Reproduced from Dolg et al. (1992c). All ionization energies are given in eV.

^b AE, all-electron results; HF, Hartree-Fock; DHF, Dirac-Hartree-Fock (spin-orbit averaged values); +QED, DHF including the Breit interaction and quantum electrodynamic corrections; WB, Wood-Boring.

^c PP, uncorrelated quasirelativistic pseudopotential calculations; a, finite difference PP calculation; b, PP calculation using an optimized (12s11p9d8f)/[9s8p6d5f] valence basis set.

Table 12 Ionization energies from quasirelativistic pseudopotential multi-reference configuration interaction calculations in comparison with experimental data⁴

Atom/ion	Configuration	Configuration LS				CPF ^{c,d}	Exp.°		
	-		0g	1g	2g	3g	4g	4g	•
Yb	4f ¹⁴ 6s ²	¹ S	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yb+	$4f^{14} 6s^1$	^{2}S	5.71	5.63	5.61	5.60	5.60	5.90	6.25
	4f ¹³ 6s ²	² F	7.97	8.15	8.43	8.66	8.85	9.11	9.45
Yb++	4f ¹⁴	^{1}S	17.35	17.21	17.18	17.22	17.19	17.59	18.44
	4f ¹³ 6s ¹	³ F	21.27	21.51	21.56	21.80	22.23	22.48	
									23.30
	$4f^{13}$ $6s^1$	¹ F	21.35	21.59	21.66	21.88	22.37	22.56	

^a Reproduced from Dolg et al. (1992c). All ionization energies are given in eV.

^b Multi-reference configuration interaction calculations (MRCI) including the Langhoff-Davidson sizeconsistency correction.

^c Coupled-pair functional calculations (CPF).

^d ng refers to a (12s11p9d8f)/[9s8p6d5f] valence basis set augmented by n g functions. Active orbitals 4f, 5s, 5p, 6s.

^e Experimental data from Martin et al. (1978).

resulting total errors of 0.40 eV and 0.50 eV, respectively, are always in favor of the states with the higher 4f occupation number. Obviously they are compensated by the errors due to neglected electron correlation effects, thus explaining the good results. It is hard to predict if a similar error cancellation occupation for the states of the corresponding [Yb 4f¹³] $\sigma_{O2p}^2 \pi_{O2p}^4 \sigma_{T}^{1} \sigma_{O2p}^{2} \pi_{O2p}^4$ superconfigurations (SCs) in the

Atom/ion	Config.	LS	J		AE re	sults ^b		PP re	sults ^c	Exp. ^d
				HF	WB	DHF	+QED	а	b	
Yb⁺	4f ¹³ 6s ²	² F	72	0	0	0	0	0	0	0
			52	11083	10329	10475	9905	10282	10434	10282
error			-	801	47	193	377	0	152	
Yb++	$4f^{13} 6s^{1}$	^{1,3} F	4	0	0	0	0	0	0	0
			3	253	305	438	423	409	352	335
			2	11088	10328	10481	9913	10288	10428	10197
			3	11444	10766	10829	10244	10617	10705	10552
Avg. error				622	125	221	226	77	134	

Table 13 Spin-orbit splittings from quasirelativistic pseudopotential calculations in comparison with all-electron results and experimental data^a

^a Reproduced from Dolg et al. (1992c). All splittings are given in cm⁻¹.

^b AE, all-electron results; HF, Hartree–Fock; WB, Wood–Boring; both with spin–orbit parameters ζ_{4f} obtained using the method of Blume and Watson; DHF, Dirac–Hartree–Fock; +QED, DHF including the Breit interaction and quantum electrodynamic corrections.

^c PP, quasirelativistic pseudopotential calculations; a, finite difference PP calculation; b, double group configuration interaction calculation using a (12s11p9d8f)/[7s6p4d3f] valence basis set.

^d Martin et al. (1978).

YbO molecule. We keep in mind that individual errors in the calculations are of the same order of magnitude as the energy separation one is interested in, i.e. 0.1 eV. The experimental atomic spin-orbit splittings, however, are reproduced in the finite basis set PP calculations with average errors of 150 cm^{-1} or less.

Since pseudopotentials will probably be used intensively in future theoretical investigations of lanthanide compounds a few comments concerning their performance are in order here. The currently available parameter sets (Dolg et al. 1989a,b, 1991d, 1993a, Cundari and Stevens 1993, Ross et al. 1994) use rather different core-valence separations. As an example for the resulting consequences we performed atomic finite-difference calculations for the excitation energies of the neutral Ce atom (table 14). Due to the rather core-like nature of the 4f shell a small core has to be used in order to avoid large frozen-core errors. Errors of 0.15 eV or less occur for the PPs which include all shells with main quantum number $n \ge 4$ in the valence space (Dolg et al. 1989a). If 4f and all shells with $n \ge 5$ are included in the valence space (Cundari and Stevens 1993) the errors increase to up to 1 eV when the 4f occupation number is changed. For energy differences between configurations with an equal 4f occupation number the errors are only a few tenth of an eV. If only the 4f, 5d (,5f, 5g) and all shells with $n \ge 6$ are included in the valence space (Ross et al. 1994) the errors increase up to several eV when the 4f occupation is changed and up to 1 eV when the 4f occupation is kept fixed. Finally, errors of 0.10 eV or less arise when the 4f shell is included in the core and only a $n \ge 5$ valence shell is treated explicitly (Dolg et al. 1989b). The energy separations between configurations

		manoo	i oon varaeo			
Configuration		PPv results ^b		AE-MCDHF ^c	PPc results ^d ,	
	Q=4	Q=12	Q=30		Q=10-12	
5d ² 6s ²	7.91	4.23	3.36	3.23	3.23	
$5d^3 6s^1$	6.90	4.40	3.37	3.24	3.23	
5d ⁴	7.44	5.59	4.46	4.33	4.29	
$4f^1 5d^1 6s^2$	0.00	0.00	0.00	0.00	0.00	
$4f^1 5d^2 6s^1$	0.19	0.68	0.67	0.66	0.64	
$4f^{1} 5d^{3}$	1.55	2.23	2.22	2.22	2.16	
$4f^2 6s^2$	1.04	2.46	1.99	2.01	2.08	
$4f^2 5d^1 6s^1$	2.17	3.59	3.22	3.24	3.23	
$4f^2 5d^2$	4.05	5.40	5.11	5.11	5.10	

Table 14 Excitation energies (eV) of Ce for the average of a nonrelativistic configuration from finite difference calculations with various ab initio pseudopotentials in comparison with all-electron multi-configuration Dirac– Hartree–Fock values^a

^a Pseudopotential calculations have been performed with the authors' extended version of the program MCHF (Froese Fischer 1977); all-electron calculations were performed with the program GRASP (Dyall et al. 1989). ^b Treatment of 4f shell in valence space. Q represents the charge of the core. Sources for pseudopotentials: Q=4, Ross et al. (1994); Q=12, Cundari and Stevens (1993); Q=30, Dolg et al. (1989a)

^c All-electron (AE) multiconfiguration Dirac-Hartree-Fock (MCDHF) calculations.

^d Treatment of 4f shell in core space. The value for the lowest configuration has been set equal to the all-electron result for each 4f subconfiguration. Source for pseudopotentials: Dolg et al. (1989b, 1991d, 1993a).

or states arising from different 4f occupation numbers may be taken from all-electron ab initio calculations or experimental data. The choice of a pseudopotential to be used in actual molecular calculations depends on the desired accuracy and on the goal of the calculation. Similar tests should be performed for the valence basis sets before e.g. energy separations between molecular states are discussed.

3.2. Diatomic molecules

3.2.1. Monohydrides

Very little experimental information is available for the monohydrides of the lanthanide elements. Their ground state configuration may be assumed to correspond to one of the following two superconfigurations (SC):

I [R 4f^{*n*}] $\sigma_{H1s}^2 \sigma_{R6s,6p}^2$ or II [R 4f^{*n*+1}] $\sigma_{H1s}^2 \sigma_{R6s,6p}^1$

The first theoretical investigations were the HF (Hartree–Fock) and DHF (Dirac– Hartree–Fock) OCE (one-center expansion) calculations for LaH ($4f^{0}\sigma^{2}\sigma^{2-1}\Sigma^{+}$ (0⁺)) and LuH ($4f^{14}\sigma^{2}\sigma^{2-1}\Sigma^{+}$ (0⁺)) by Pyykkö (1979b). The calculated bond lengths (LaH: HF 2.21 Å, DHF 2.22 Å; LuH: HF 2.02 Å, DHF 2.01 Å) and vibrational frequencies (LaH: HF 1390 cm⁻¹, DHF 1402 cm⁻¹; LuH: HF 1548 cm⁻¹, DHF 1557 cm⁻¹) indicate rather

Molecule	n(4f) ^b	Method ^c	De	(eV)	R_{c} (Å)	$\omega_{\rm e}$ (cm ⁻¹)	μ_{e} (D)
	. ,		calc.	exp.d	calc.	exp. ^d	calc.	exp. ^d	calc.
LaH	0	a, c	2.42		2.075		1365		2.86
		b, c	2.57		2.089		1371		
		b, d	2.71		2.085		1450		
	$\geqslant 0$	b, e	3.01		2.005		1461		
CeH	1	a, c	2.43		2.056		1375		2.78
PrH	2	a, c	1.88		2.042		1385		2.68
NdH	4	a, c	1.63		2.257		1133		2.97
PmH	5	a, c	1.59		2.247		1131		2.97
SmH	6	a, c	1.57		2.241		1136		2.94
EuH	7	a, c	1.55		2.235		1149		2.89
		b, c	1.23		2.232		1102		
		b, d	1.59		2.203		1151		
	≥7	b, e	1.82		2.150		1215		
GdH	7	a, c	2.52		1.989		1417		2.16
ТЬН	8	a, c	2.52		1.986		1409		2.06
DyH	9	a, c	1.65		1.980		1415		1.96
НоН	10	a, c	1.58		1.975		1426		1.87
ErH	11	a, c	1.77		1.969		1422		1.79
TmH	13	a, c	1.37		2.169		1144		2.86
YbH	14	a, c	1.35	≤1.63	2.179	2.053	1167	1250	2.81
		b, c	1.01		2.156		1153		
		b, d	1.35		2.132		1189		
		b, e	1.57		2.089		1282		
LuH	14	a, c	2.79	~3.47	1.958	1.912	1427	1500	1.58
		b, c	3.24		1.973		1374		
		b, d	3.24		1.954		1445		
		b,e	3.47		1.936		1493		

Table 15

Binding energies D_e , bond lengths R_e , vibrational frequencies ω_e and dipole moments μ_e for the lanthanide monohydrides from configuration interaction calculations including the Langhoff–Davidson size-consistency correction in comparison with experimental data^a

^a Data from Dolg and Stoll (1989) and Dolg (1995).

^b n(4f), the 4f occupation number modeled by the lanthanide pseudopotential.

^c (a) nonrelativistic pseudopotential;

(b) quasirelativistic pseudopotential;

(c) basis sets: R (7s6p5d)/[5s4p3d], H (5s1p)/[3s1p];

(d) basis sets: R (7s6p5d2f)/[5s4p3d2f], H (10s5p1d)/[5s3p1d];

(e) basis sets: R (8s7p6d6f), H (8s4p3d2f).

^d Experimental data from Huber and Herzberg (1979); the binding energies D_e have been derived from the dissociation energies D_0 by adding an estimate for the zero-point vibration energy; the value given for LuH is actually for LuD.



Fig. 7. Linear behavior of the binding energies D_e of the lanthanide monohydrides for fixed 4f occupation number. Data taken from Dolg and Stoll (1989).

small relativistic effects. The binding energies derived from a Morse potential fit were significantly overestimated and will not be discussed here.

Dolg and Stoll (Dolg 1989, 1995, Dolg and Stoll 1989, Dolg et al. 1989c) performed pseudopotential (PP) calculations at the SCF (self-consistent field) and CISD (singlereference configuration interaction with single and double excitations; the Langhoff-Davidson (1974) size-consistency correction has been applied) level for the above given SCs with an inclusion of the 4f shell into the PP core. Most of the results have been obtained with nonrelativistic PPs and small basis sets without f functions on the lanthanide atoms. However, corresponding relativistic results obtained with larger basis sets are available for LaH and LuH for SC I, and for EuH and YbH for SC II. The most important results are summarized in table 15. Relativistic effects in the valence shell are found to lead to small bond-length expansions of up to 0.02 Å and a bond stabilisation (0.15 eV for LaH, 0.45 eV for LuH) for SC I, whereas small bond-length contractions of up to 0.02 Å and a bond destabilisation (0.32 eV for EuH, 0.34 eV for YbH) are observed for SC II. The binding energies calculated for YbH and LuH are in excellent agreement with the available experimental data from Huber and Herzberg (1979) (YbH: calc. 1.57 eV, exp. ≤ 1.63 or 2.00 eV, LuH: calc. 3.47 eV, exp. ~ 3.47 eV for LuD). The vibrational frequencies are also well reproduced (YbH: calc. 1282 cm⁻¹, exp. 1250 cm⁻¹, LuH: calc. 1493 cm⁻¹, exp. 1500 cm⁻¹), whereas the calculated bond lengths are slightly too long (YbH: calc. 2.089 Å, exp. 2.053 Å, LuH: calc. 1.936 Å, exp. 1.912 Å).

Keeping in mind the almost linear variation of the binding energies when calculated with respect to dissociated atoms with the lanthanide in the lowest state with the same 4f occupation as in the molecule (fig. 7), one may use these data to intrapolate or extrapolate the corresponding results for other molecules. The characteristic nonmonotonic 'saw-tooth' behavior results from cases where the 4f occupation number in the atom and the molecule do not agree and parallels the atomic excitation energies (fig. 4). The results of such a linear intrapolation using the best available CISD data (b, e in table 15) for LaH



Fig. 8. Binding energies D_e for the two low-lying superconfigurations (SC) (I, $4f^n\sigma^2\sigma^2$; II, $4f^{n+1}\sigma^2\sigma^1$) of the lanthanide monohydrides. Extrapolated theoretical values for pseudopotential configuration interaction calculations based on the b, e entries in table 15.

and LuH (SC I) as well as EuH and YbH (SC II) are summarized in fig. 8. If only the two SCs given above are considered to be low-lying in energy, the ground states of LaH–NdH, GdH–ErH and LuH should result from the first and those of SmH–EuH and YbH from the second SC, whereas PmH and TmH appear to be borderline cases.

The electronic states of the lanthanum hydrides LaH (Das and Balasubramanian 1990) and LaH₂ (Das and Balasubramanian 1991a) as well as their cations LaH⁺ and LaH₂⁺ (Das and Balasubramanian 1991b) have been studied using a quasirelativistic effective core potential and basis sets of various sizes for La with CASSCF [complete active space (multi-configuration) self-consistent field] and subsequent FOCI (first-order configuration interaction) and SOCI (second-order configuration interaction) calculations. Spin-orbit effects were derived from RCI (relativistic configuration interaction) calculations for the diatomic molecules. Since these calculations have been reviewed in detail by Balasubramanian (1994), we will not discuss them here further.

Dolg et al. (1992b) investigated YbH using a Yb⁴²⁺ [Ar 3d¹⁰] core PP for Yb and large basis sets including up to four g functions on Yb. The results of SCF and MRCI calculations in the AS coupling scheme are summarized in table 16. The spectroscopic constants of the X ${}^{2}\Sigma^{+}$ ground state are in excellent agreement with the experimental values. Spin-orbit interaction was also included by means of the Columbus DGCI (double group configuration interaction) code (A.H.H. Chang and Pitzer 1989). The $\Omega = \frac{1}{2}$ lowest excited state (57% ${}^{2}\Sigma^{+}$, 43% ${}^{2}\Pi$) of the 4f¹³ $\sigma^{2}\sigma^{2}$ SC is located 10456 cm⁻¹ above the 4f¹⁴ $\sigma^{2}\sigma^{1}$ X ${}^{2}\Sigma^{+}$ $\Omega = \frac{1}{2}$ ground state, when the best AS coupled MRCI results were corrected for spin-orbit effects derived from DGCI calculations. We note that the correlation contribution to this energy separation is 1.48 eV and 2.33 eV without and with g functions on Yb, respectively. Moreover, without any correlation effects the ground state would be predicted to arise from the 4f¹³ $\sigma^{2}\sigma^{2}$ SC. For a discussion of higher excited states we refer to the original paper. From ESR (electron spin resonance) spectroscopy Van Zee et al. (1977) deduced that bonding in YbH is largely that of an ion pair Yb⁺H⁻

ELECTRONIC STRUCTURE CALCULATIONS

Table 16Molecular constants for the $4f^{14}\sigma^2\sigma^1 X {}^{2}\Sigma^{+}$ ground state and the $4f^{13}\sigma^2\sigma^2 A {}^{2}\Sigma^{+}$ excited state of YbH from multi-
reference configuration interaction calculations including the Langhoff–Davidson size-consistency correction
(MRCI)^a

State	Method	Basis	$R_{\rm e}$ (Å)	D_{e} (eV)	$\omega_{e} (cm^{-1})$	μ_{e} (D)
X ² Σ ⁺	MRCI (SCF)	0g	2.079 (2.135)	1.52 (1.22)	1265 (1227)	2.75 (2.93)
		4g	2.074 (2.135)	1.51 (1.22)	1276 (1228)	2.74 (2.92)
	exp. ^b	-	2.053	≤1.63	1250	
$A^{2}\Sigma^{+}$	MRCI (SCF)	0g	1.900 (1.953)	0.49 (1.97)	1560 (1513)	0.97 (1.08)
		4g	1.890 (1.953)	-0.31 (2.02)	1556 (1511)	0.93 (1.08)

^a After Dolg et al. (1992b).

Self-consistent field (SCF) results in parentheses. Yb: (12s11p9d8f)/[9s8p6d5f] augmented with *n* g functions; quasirelativistic Yb⁴²⁺ [Ar 3d¹⁰] core PP; H: (8s2p)/[5s2p]. ^b Experimental data from Huber and Herzberg (1979); the D_e values have been obtained from the experimental D_0 results by adding the zero-point vibration energy.

Table 17

Binding energies D_e , bond lengths R_e , vibrational frequencies ω_e and dipole moments μ_e for the ground states of selected lanthanide monohydrides from relativistically corrected density-functional studies in comparison with experimental data

Molecule	$D_{\rm e}~({\rm eV})$		R _e	(Å)	ω_{e} (c	μ_{e} (D)	
	calc. ^a	exp. ^b	calc. ^a	exp. ^b	calc. ^a	exp. ^b	calc.
LaH	2.99		2.08		1378	1.1.1.1.1.PP.	2.82
GdH	2.67		1.99		1507		2.38
ҮЬН	1.58	≤1.63	2.08	2.053	1193	1250	3.12
LuH	3.20	~3.47	1.89	1.912	1567	1500	1.90

^a Calculation results from Wang and Schwarz (1995).

^b Data from Huber and Herzberg (1979); binding energies D_e have been derived from dissociation energies D_0 by adding an estimate for the zero-point vibration energy; the value given for LuH is actually for LuD.

and less than 20% of the spin density is on H. This is consistent with the results of a SCF Mulliken population analysis, where 97% of the unpaired electron is assigned to Yb (Yb s 68%, p 28%, d 1%, H s 3%). The singly occupied orbital is strongly polarized away from H yielding a contribution of -4.8 D to the SCF dipole moment of 2.9 D. The doubly occupied bonding σ orbital is mainly localized on H (Yb s 13%, p 5%, d 5%, H s 77%).

During the completion of the present review we became aware of all-electron frozencore (R $1s^2 \cdots 4d^{10}$) QR-DFT (quasirelativistic density-functional theory) calculations for selected lanthanide diatomics by Wang and Schwarz (1995). Results obtained with the Amsterdam program (Snijders and Baerends 1978, Snijders et al. 1979), gradientcorrected exchange (Becke 1988) and self-interaction corrected (Stoll et al. 1978, 1980) correlation (Vosko et al. 1980) energy functionals are summarized in table 17. The agreement with experimental data is quite satisfactory.

3.2.2. Monoxides

The monoxides of the lanthanide elements seem to be the most extensively investigated ones of the diatomic molecules reviewed here, both experimentally and theoretically. Most of the available theoretical studies have already been reviewed by Balasubramanian (1994). These are mainly INDO/S-CI (spectroscopic version of the intermediate neglect of differential overlap method with spin-orbit configuration interaction) and PP SCF/CISD/MRCI (pseudopotential self-consistent field and subsequent single- or multireference configuration interaction) calculations of the Munich and Stuttgart groups, respectively. Some of the PP calculations also account for spin-orbit effects. Recently results of QR-DFT (quasirelativistic density-functional theory) studies also became available (Wang et al. 1995). In addition a number of LFT (ligand field theory) model calculations have been published (Dulick et al. 1986, Carette and Hocquet 1988). We will restrict ourselves to outline the general trends in the series from LaO through LuO and discuss in more detail only some selected molecules, i.e. LaO, CeO, EuO, GdO, YbO and LuO. For none of the other molecules calculations with an explicit treatment of the 4f shell are available to our knowledge.

The ground state configuration of the lanthanide monoxides may be assumed to arise from either of the two superconfigurations (SC):

I [R 4f^{*n*}]
$$\sigma_{O2p}^2 \pi_{O2p}^4 \sigma_{R6s,6p}^1$$
 or II [R 4f^{*n*+1}] $\sigma_{O2p}^2 \pi_{O2p}^4$.

According to all studies bonding in the lanthanide monoxides can be considered to be rather ionic, the limiting form being a $R^{2+}O^{2-}$ ion pair. The R^{2+} ion is either in a $4f^{n}6s^{1}$ or a $4f^{(n+1)}$ configuration. It was soon recognized that the nonmonotonic variation in the binding energies (fig. 9) closely parallels the excitation energies of the $4f^{n+1} \rightarrow 4f^{n}5d^{1}$ and $4f^{n+1}6s^{2} \rightarrow 4f^{n}5d^{1}6s^{2}$ electronic transitions of the divalent ions (Ames et al. 1967) and neutral atoms (Murad and Hildenbrand 1980) (fig. 4), respectively. This so-called 'promotional model' for the lanthanide monoxides assumes ground states belonging to the SC I for all molecules except for EuO and YbO, where due to a stable half-filled or filled 4f shell the ground state should result from SC II (Field 1982). The vibrational frequencies of, respectively, $830\pm20 \text{ cm}^{-1}$ and $680\pm20 \text{ cm}^{-1}$ should be characteristic for the SCs, independent of the individual electronic state. Changes in the bond lengths along the series should also be diagnostic for the ground state. For Eu²⁺ and Yb²⁺ the $\langle r \rangle$ expectation values of the 5p shell are larger by 0.030 Å and 0.025 Å, respectively, for the $4f^{n+1}$ configuration than for the $4f^{n}6s^{1}$ configuration. The average value for the lanthanide contraction per element is about 0.01 Å or smaller.

The ground-state properties of all the diatomic monoxides of the lanthanide series have been studied at the SCF/CISD level with PPs that attribute the open 4f shell to the core (Dolg 1989, 1995, Dolg and Stoll 1989, Dolg et al. 1989c). The results of these studies are summarized in table 18. It was found that the nonmonotonic trend in the experimental binding energies is quite well reproduced by the theoretical values (fig. 9) and that the vibrational frequencies are in reasonable agreement with the available experimental values, however the calculated bond lengths were found to be too large at



Fig. 9. Binding energies for the low-lying superconfigurations (SC) (I, $4f^n\sigma^2\pi^4\sigma^1$; II, $4f^{n+1}\sigma^2\pi^4$) of the lanthanide monoxides. Extrapolated theoretical values for pseudopotential configuration interaction calculations based on the b, e entries in table 18.

the beginning of the series. For LaO $R_e = 1.952$ Å and $D_e = 6.42$ eV was obtained when the f PP was adjusted to guarantee a fixed $4f^0$ subconfiguration on La, whereas $R_e = 1.894$ Å and $D_e = 6.89 \text{ eV}$ was calculated at the same level of theory when this restriction was abandoned. The experimental values are $R_e = 1.826$ Å (Bernard and Sibai 1980) and $D_0 = 8.24 \pm 0.04 \text{ eV}$ (Dulick et al. 1986). The difference between the two PP results, i.e. $\Delta R_{\rm e} = -0.06$ Å and $\Delta D_{\rm e} = 0.5$ eV, may be attributed to a participation of the 4f orbitals in chemical bonding. Agreement with experimental data is considerably better at the end of the series than at the beginning, e.g. for LuO the theoretical results $R_e = 1.800$ Å and $D_e = 6.12 \text{ eV}$ are closer to the experimental values $R_e = 1.790 \text{ Å}$ (Bernard and Effantin 1986) and $D_0 = 6.99 \pm 0.08 \text{ eV}$ (Dulick et al. 1986). We must conclude from these results that the 4f orbitals of the lighter lanthanide elements indeed contribute to chemical bonding, whereas they have a core-like character as suggested by the SC model of Field (1982) for the heavier lanthanide elements. We note here that too long a bond length for LaO is also obtained with the effective core potential published by Hay and Wadt (1985b), i.e. $R_e = 1.889$ Å and $D_e = 6.83$ eV (Dolg and Stoll 1989, Dolg et al. 1989c). The remaining error was found to be due to a lack of tight f basis functions: using an allelectron f basis set the values $R_e = 1.947$ Å and $R_e = 1.831$ Å were obtained for integral and nonintegral 4f occupation numbers, respectively (Dolg 1989). The calculated values for the lanthanide contraction are 0.16 Å and 0.04 Å without and with 4f orbital participation, respectively. The latter value essentially agrees with experimental data.

The role of the 4f orbitals at the CI level was further investigated for La and LaO (Dolg 1989). The CI wavefunction of the La ²D ground state is characterized by a leading $5d^{1}6s^{2}$ reference configuration with $6s^{2} \rightarrow 6p^{2}$ and $5p^{6} \rightarrow 5p^{5}4f^{1}$ excitations accounting for near

Table	18
-------	----

Binding energies D_e , bond lengths R_e , vibrational frequencies ω_e and dipole moments μ_e for the lanthanide monoxides from configuration interaction calculations including the Langhoff–Davidson size-consistency correction in comparison with experimental data^a

Molecule	<i>n</i> (4f) ^b	Method ^c	De	(eV)	$R_{\rm e}$ ((Å)	ω, (cm ⁻¹)	$\mu_{\rm e}$ (D)
			calc.	exp.d	calc.	exp.d	calc.	exp.d	calc.
LaO	0	a, c	5.84	8.29	1.999	1.826	759	813	3.78
		b, c	5.48		2.009		818		4.94
		b, d	6.42		1.952		829		3.96
	$\geqslant 0$	b, e	8.02		1.813		847		2.58
CeO	1	a, c	5.87	8.27	1.974	1.820	763	828	3.80
PrO	2	a, c	5.29	7.79	1.964	1.801	769	822	3.86
NdO	3	a, c	4.99	7.27	1.951	1.803	768	815	3.93
PmO	4	a, c			1.938		775		3.97
SmO	5	a, c	3.58	5.82	1.927		776	808	4.05
EuO	6	a, c	2.46		1.917		776		4.15
		b, c	2.12		1.920		782		5.41
		b, d	2.99		1.867		850		4.57
	7	a, c	3.18	4.96	2.004		676	668	9.99
		b, c	2.43		2.015		671		10.30
		b, d	3.31		1.955		682		9.79
	≥7	b, e	4.09		1.888		680		9.43
GdO	7	a, c	5.78	7.44	1.908	1.812	780	828	4.25
TbO	8	a, c	5.72	7.38	1.897	1.814	784	824	4.34
DyO	9	a, c	4.80	6.29	1.889	1,796	776	829	4.44
HoO	10	a, c	4.68	6.34	1.882	1.799	784	829	4.52
ErO	11	a, c	4.81	6.36	1.875		785	829	4.65
TmO	12	a, c	4.05	5.21	1.868		789	832	4.74
YbO	13	a, c	2.79		1.863		797		4.87
		b, c	2.37		1.863		749		6.04
		b, d	3.22		1.807		849		5.61
	14	a, c	2.40	4.11	1.978	1.807	684	683	8.56
		b, c	1.78		2.015		568		8.18
		b, d	2.14		1.929		624		8.05
		b, e	2.98		1.920		612		10.58
LuO	14	a, c	5.63	7.04	1.858	1.790	789	842	4.99
		b, c	5.28		1.852		828		6.31
		b, d	6.12		1.800		852		5.57
		b, e	6.49		1.790		861		5.73

^a Data from Dolg and Stoll (1989) and Dolg (1995).

^b n(4f), the 4f occupation number modeled by the lanthanide pseudopotential.

^c (a) nonrelativistic pseudopotential;

(b) quasirelativistic pseudopotential;

(c) basis sets: R (7s6p5d)/[5s4p3d], O (9s6p)/[4s3p];

(d) basis sets: R (7s6p5d2f)/[5s4p3d2f], O (9s6p2d)/[4s3p2d];

(e) basis sets: R (8s7p6d6f), O (13s7p4d3f2g).

^d Only a selection of the data for R_e and ω_e summarized in Dolg and Stoll (1989) has been reproduced; the binding energies D_e have been derived from the dissociation energies D_0 listed by Dulick et al. (1986) by adding an estimate for the zero-point vibration energy (0.04 eV for EuO and YbO, 0.05 eV elsewhere).

Orbital energy (eV)	Symmetry	Occupation	Composition
-34.36	σ	2	0.93 O 2s + 0.28 Ce 5d + 0.19 Ce 6p + 0.15 Ce 6s
-13.49	π	4	0.87 O 2p + 0.47 Ce 5d + 0.12 Ce 6p
-12.62	σ	2	0.93 O 2p - 0.29 Ce 5d - 0.15 Ce 4f + 0.15 Ce 6p
-10.36	ф	2	1.00 Ce 4f
-10.26	δ	27	1.00 Ce 4f
-10.16	π	$\frac{2}{7}$	0.98 Ce 4f
-10.05	σ	17	0.97 Ce 4f – 0.23 Ce 5d
-6.30	σ	1	0.95 Ce 6s – 0.24 Ce 5d – 0.20 Ce 6p
-5.24	δ	0	1.00 Ce 5d
-3.95	π	0	0.92 Ce 6p – 0.37 Ce 5d + 0.11 O 2p
-3.26	σ	0	0.80 Ce 6p - 0.50 Ce 5d - 0.30 O 2p

Table 19 Analysis of the molecular orbitals for the $4f^1\sigma^2\pi^4\sigma^1$ SC of CeO from INDO calculations^a

^a Calculations from Kotzian et al. (1992). For the composition of the orbitals only contributions with coefficients exceeding 0.1 are listed.

degeneracy and core polarisation effects, respectively, as the next important contributions. In case of the ${}^{2}\Sigma^{+}$ ground state of LaO one finds besides the leading ionic reference configuration $La^{2+}\sigma^{1}_{La6s,6p} O^{2-}\sigma^{2}_{O2p}\pi^{4}_{O2p}$ important contributions of $\pi^{4}_{O2p} \rightarrow \pi^{2}_{O2p}\delta^{2}_{O3d}$ and $\pi^{4}_{O2p} \rightarrow \pi^{2}_{O2p}\pi^{2}_{La4f}$ excitations describing local angular correlation on oxygen and charge-transfer $La^{2+}O^{2-} \rightarrow LaO$, respectively.

An analysis of the molecular valence orbitals derived from semiempirical INDO calculations for an average of the SC (Kotzian et al. 1992) is listed in table 19. It is evident that the 4f shell as a whole approximately keeps an atomic character in the molecular environment, however a notable mixing with the 5d orbitals is observed for the σ symmetry.

The above discussion shows that, although the SC model is qualitatively appealing and quite useful in practice to reduce the necessary computational effort for quantumchemical studies of lanthanide compounds, it needs some improvement for quantitative work when using PPs that include the 4f shell in the core. An attempt in this direction has been made recently (Dolg et al. 1993a). The f PPs were readjusted to also allow nonintegral 4f occupation numbers q, e.g. $n \le q < n+1$ for trivalent and $n+1 \le q < n+2$ for divalent lanthanide atoms in molecules. The agreement between theory and experiment is considerably improved upon this simple modification of the parameter sets. Table 20 compares results from SCF/CISD calculations on CeO with PPs modeling an integral or nonintegral 4f occupation number with more rigorous ab initio PP SCF/CISD calculations that explicitly treat the 4f shell in the valence space (Dolg et al. 1991a).

The molecules LaO, GdO and LuO have been studied by Kotzian et al. (1992) in INDO/S-CI calculations. These three molecules are formally related since they have ground-state electron configurations with an empty, half-filled and filled 4f shell yielding

State	Space ^b	R _e	(Å)	De	(eV)	$T_{\rm e}$ (eV)	ω, (α	
	- ·	calc. °	exp.	calc. °	exp.	calc. ^c	calc. ^c	exp.
³ Ф	v	1.827	1.820	7.28	8.22	0.00	838	824
${}^{1}\Phi$	v	1.827				0.04	837	
$^{3}\Delta$	v	1.819				0.10	840	
$^{1}\Delta$	v	1.818				0.15	836	
³ Π	v	1.819				0.17	833	
$^{1}\Pi$	v	1.826				0.21	829	
3Σ	v	1.816				0.18	835	
$^{1}\Sigma$	v	1.817				0.31	834	
Avg.	v	1.821	1.811	7.16	7.94		836	823
Avg. ^d	с	1.819		7.25			834	
Avg. ^e	с	1.926		6.34			822	

^a Data taken from Dolg et al. (1991a, 1993a).

^b v, 4f shell in valence space; c, 4f shell in core space.

^c Results from quasirelativistic pseudopotential configuration interaction calculations including the Langhoff-Davidson size-consistency correction.

Ce (v): PP with 30 valence electrons, (12s11p9d8f)/[9s8p6d5f] basis;

Ce (c): PP with 11 valence electrons;

O: (9s6p1d)/[4s3p1d] basis.

^d 4f occupation number $n(4f) \ge 1$, (7s6p5d4f)/[5s4p3d4f] basis.

^e 4f occupation number n(4f) = 1, (7s6p5d2f)/[5s4p3d2f] basis.

 ${}^{2}\Sigma^{+}$ (LaO, LuO) and ${}^{9}\Sigma^{-}$ (GdO) ground states. The authors discuss the electronic structure of the ground state and excited states with term energies approximately up to 50000 cm⁻¹ (LaO, LuO) or 25000 cm⁻¹ (GdO) and give values for transition energies as well as oscillator strengths, Based on these data the authors attempt the assignment of several experimentally observed higher excited states. All calculations were carried out for the experimental bond distances of the ground state. No attempts have been made to optimize bond lengths or to calculate the vibrational frequencies or binding energies. The results of a Mulliken population analysis for the ground state SCs are summarized in table 21. Obviously the ionic character increases from LaO to LuO. This is in agreement with the trend in the dipole moments from the PP calculations listed in table 18. Compared to the purely ionic metal configuration R^{2+} 4fⁿ6s¹ the metal accepts charge from the O²⁻ anion through the σ and π orbitals. This formally leads to a R⁺ 4fⁿ5d¹6s¹ configuration of the metal, which is however misleading since there is no occupied molecular orbital with predominantly R 5d character. The occupation of the 6s orbital is reduced via the mixing with the 6p and 5d orbitals in σ symmetry. The admixture of 6p leads to an orbital polarized away from O. From the f occupation numbers one may assume that a small f-

	calculatio	JIIS WITH G				calculation		
Method	Molecule	R 6s	R 6p	R 5d	R 4f	O 2s	О 2р	Charge on R
INDO	LaO	0.95	0.15	1.14	0.07	1.92	4.78	0.70
INDO	GdO	0.90	0.12	1.13	7.03	1.95	4.87	0.82
INDO	LuO	0.94	0.09	1.12	13.99	1.95	4.92	0.87
QR-DFT	LaO	0.77	0.17	1.15	0.38	1.94	4.60	0.53
QR-DFT	GdO	0.88	0.23	0.66	7.74	1.98	4.51	0.49
PP SCF	GdO	0.83	0.15	1.04	7.08	1.90	5.00	0.90

Table 21 Comparison of Mulliken population analysis for the $4f^{n}\sigma^{2}\pi^{4}\sigma^{1}$ SC of LaO, GdO and LuO from INDO calculations^a with data from QR-DFT^b and PP SCF calculations^c

^a INDO (intermediate neglect of differential overlap) calculations, Kotzian et al. (1992).

^b QR-DFT (quasirelativistic density-functional) calculations, Wang et al. (1995).

^c PP SCF (pseudopotential self-consistent field) calculations, Dolg et al. (1990a).

orbital participation in bonding is present for LaO, whereas the 4f shell has core character in LuO.

The term energies of the $^{2}\Delta$ and $^{2}\Pi$ excited states of LaO were calculated by Kotzian et al. (1992) to be 8842 cm⁻¹ and 14290 cm⁻¹ in good agreement with the experimental values (Carette 1990) of 7819 cm⁻¹ and 13067 cm⁻¹, respectively. The corresponding theoretical results for LuO are $19140 \,\mathrm{cm}^{-1}$ and $24862 \,\mathrm{cm}^{-1}$. The agreement with the experimental (Huber and Herzberg 1979) value of 20431 cm⁻¹ for the $^{2}\Pi$ state is still in the range of accuracy one may expect for an ab initio calculation of medium quality. The authors used the spin-orbit splittings of these states to adjust the parameters ζ_{5d} and ζ_{6D} of their method. Due to lack of experimental data the former value for Lu was derived from the spectrum of LuF, however. The findings of Kotzian et al. for LaO should be useful for the interpretation of the experimental spectrum. Berg et al. (1965) proposed that the lowest energy excited ${}^{2}\Pi$ state arises from a 6p¹ configuration on La²⁺, whereas Kaledin et al. (1993), who where obviously unaware of any theoretical work, proposed on the basis of LFT that the 5d¹ configuration is involved. In view of the excellent INDO/S-CI results the interpretation of Berg et al. seems to be more likely. If the results of Kotzian et al. are correct the configurational assignments of the higher excited electronic states of CeO based on the analogy to LaO by Kaledin et al. have to be viewed with some caution.

The low-lying electronic states of LaO and LaO⁺ have recently been studied at the CASSCF level by Márquez et al. (1994) using the La PP of Hay and Wadt (1985b) and basis sets of double zeta quality. The results suffer somewhat from the limited basis sets, e.g. the calculated bond length for the LaO ${}^{2}\Sigma^{+}$ ground state ($R_{e} = 1.987$ Å) is significantly larger than the experimental value ($R_{e} = 1.826$ Å). The agreement of the calculated term energies of the excited states with experimental data (which the authors were not aware of) is modest. (We note that the low-lying ${}^{2}\Pi$ state discussed above has probably been

compans	and vibrational frequencies ω_e of the $4f^7\sigma^2\pi^4\sigma^1 X^9\Sigma^-$ and $4f^7\sigma^2\pi^4\sigma^1 A^7\Sigma^-$ states of GdO. ⁴											
State	Space ^b	$R_{\rm e}$ (Å)		De	(eV)	$T_{\rm e}$ (eV) $\omega_{\rm e}$		ω, ((cm ⁻¹)			
		calc. ^c	exp. ^d	calc. ^c	exp. ^d	calc. °	exp. ^d	calc. ^c	exp. ^d			
X °Σ-	v	1.822	1.812	6.37	7.44 ±0.10	0.00	0.00	845	824			
A ⁷ Σ-	v	1.820	1.805			0.23	0.23	849				
Avg. ^e	с	1.801		6.62				820				
Avg. ^f	с	1.855		6.14				829				

Table 22 Comparison of calculations and experimental results for the bond lengths R_e , binding or term energies D_e , T_e , and vibrational frequencies ω_e of the $4f^{\gamma}\sigma^2\pi^4\sigma^1 X^9\Sigma^-$ and $4f^{\gamma}\sigma^2\pi^4\sigma^1 A^{\gamma}\Sigma^-$ states of GdO.^a

^a Data taken from Dolg et al. (1990a, 1993a).

^b v, 4f shell in valence space; c, 4f shell in core space.

^c Results from quasirelativistic pseudopotential configuration interaction calculations including the Langhoff-Davidson size-consistency correction.

Gd (v): PP with 36 valence electrons, (12s11p9d8f)/[9s8p6d5f] basis;

Gd (c): PP with 11 valence electrons;

O: (9s6p1d)/[4s3p1d] basis.

^d Experimental values from DeKock and Weltner (1971), Yadav et al. (1981), Dulick et al. (1986), Carette et al. (1987), Kaledin et al. (1994). For D_e , the zero-point vibration energy has been added to the experimental dissociation energy D_0 .

^e 4f occupation number $n(4f) \ge 7$, (7s6p5d4f)/[5s4p3d4f] basis.

^f 4f occupation number n(4f) = 7, (7s6p5d2f)/[5s4p3d2f] basis.

overlooked.) The calculated ionization potential of 5.16 eV is close to the experimental value of $4.95\pm0.1 \text{ eV}$ (Ackermann et al. 1976).

In the case of GdO the electronic states below 20000 cm^{-1} arise similarly to LaO and LuO from ${}^{2}\Sigma^{+}$, ${}^{2}\Delta$ and ${}^{2}\Pi$ valence substates. However, the situation is more complicated since these are coupled to a 4f⁷ ${}^{8}\Sigma^{-}$ (${}^{8}S$) subshell, yielding nonet and septet states of Σ^{-} , Δ and Π symmetry which are further split by spin-orbit interaction (Carette et al. 1987). Kotzian et al. (1992) calculated the term energies for all these levels and compared their results to the few available experimental values. Experimentally the ${}^{9}\Sigma^{-}$ ground state (Van Zee et al. 1981) and the ${}^{7}\Sigma^{-}$ first excited state are separated by only 1840 cm⁻¹ (Carette et al. 1987, Kaledin et al. 1994). Both states result mainly from the coupling of the $\sigma^{2}\pi^{4}\sigma^{1}{}^{2}\Sigma^{+}$ valence substate to the 4f⁷ ${}^{8}\Sigma^{-}$ (${}^{8}S$) core substate. The INDO/S-CI result for the energy separation of 1166 cm⁻¹ is only 63% of the experimental value. According to Kotzian et al. both states are pure $\Lambda\Sigma$ states, i.e. spin-orbit effects are negligible, and all other states are more than 1 eV higher in energy.

Prior to the INDO/S-CI calculations of Kotzian et al. the two lowest electronic states of GdO have also been studied by Dolg et al. (1990a) with quasirelativistic PP SCF/CISD calculations (table 22). The spectroscopic constants for the ground state ($R_e = 1.822$ Å, $D_e = 6.37$ eV, $\omega_e = 845$ cm⁻¹) are in good agreement with experimental data ($R_e = 1.812$ or 1.808 Å, $D_0 = 7.39 \pm 0.10$ eV, $\omega_e = 824$ cm⁻¹). When the destabilization of the bond due to spin–orbit effects in the Gd $4f^75d^16s^2$ 9D_2 ground state is considered, one obtains

Molecule	<i>D</i> _e (eV)		R _e	(Å)	ω _e (cm ⁻¹)	μ_{e} (D)	
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	
LaO	7.60	8.29	1.89	1.826	761	813	3.73	
EuO	5.19	4.92	1.89	(1.89)	675	672	6.57	
GdO	6.68	7.44	1.82	1.812	810	828	2.90	
YbO	4.06	4.11	1.93	1.807	615	683	7.60	
LuO	6.94	7.04	1.83	1.790	796	842	4,58	

Table 23

Binding energies D_e , bond lengths R_e , vibrational frequencies ω_e and dipole moments μ_e for the ground states of selected lanthanide monoxides from relativistically corrected density-functional studies in comparison with experimental data^a

^a Calculations from Wang and Schwarz (1995) and Wang et al. (1995).

Only a selection of the experimental data for R_e and ω_e summarized by Dolg and Stoll (1989) has been reproduced; the binding energies D_e have been derived from the dissociation energies D_0 listed by Dulick et al. (1986) by adding an estimate for the zero-point vibration energy (0.04 eV for EuO and YbO, 0.05 eV elsewhere).

 $D_e = 6.17 \text{ eV}$ (84% of the experimental dissociation energy). The splitting between the ${}^9\Sigma^-$ and ${}^7\Sigma^-$ is calculated as 1887 cm⁻¹ in excellent agreement with the experimental result of 1840 cm⁻¹. A Mulliken population analysis of the ground state SCF wavefunction yields a charge distribution Gd^{0.90+} 4f^{7.08}5d^{1.04}6s^{0.83}6p^{0.15} O^{0.90-} 2s^{1.90}2p^{5.00} in reasonable agreement with the state-averaged INDO results of Kotzian et al. (table 21). Seven of the eight unpaired electrons are found, in accordance with Field's SC model, to occupy the 4f orbitals on Gd to more than 99%. The eighth unpaired electron is in the σ valence orbital which is to 95% localized on Gd. The dominant contribution stems from the Gd 6s orbital (81%), whereas smaller ones result from the Gd 6p (11%) and 5d (3%) orbitals. These findings are in line with the LFT results of Carette et al. (1987) but they do not support the interpretation of ESR spectra by Van Zee et al. (1981) who concluded that the main contributions to this singly occupied orbital come from the Gd 5d orbital.

Wang and Schwarz (1995) and Wang et al. (1995) used the relativistically corrected density-functional approach of the Amsterdam group (Snijders and Baerends 1978, Snijders et al. 1979) together with a gradient corrected exchange (Becke 1988) and a self-interaction corrected correlation (Vosko et al. 1980, Stoll et al. 1978, 1980) energy functional to study LaO, EuO, GdO, YbO and LuO (table 23). The results for the ground state of GdO ($R_e = 1.82 \text{ Å}$, $D_e = 6.68 \text{ eV}$, $\omega_e = 810 \text{ cm}^{-1}$) are in excellent agreement with experimental data ($R_e = 1.822 \text{ Å}$, $D_e = 7.44 \text{ eV}$, $\omega_e = 824 \text{ cm}^{-1}$). A Mulliken population analysis reflects a lower ionicity than derived from the PP calculations discussed above, i.e. $\text{Gd}^{0.49+}$ 4f^{7.74}5d^{0.66}6s^{0.88}6p^{0.23} O^{0.49-} 2s^{1.98}2p^{4.51} (table 21). This is mainly due to the relatively high 4f occupation number. The errors in the bond lengths and vibrational frequencies for LaO and LuO are somewhat larger than for GdO.

Between CeO, EuO, TbO and YbO also a formal relationship exists. One may imagine that the ground state SCs of CeO (Linton et al. 1983b) and TbO (Kulikov et al. 1984)

Ω		Term energ	gies (cm ⁻¹))	Vibrati	onal const.	(cm ⁻¹)	Rotation	al const. (1	$0^{-4} \mathrm{cm}^{-1}$)
	exp. ^a ,	INDO ^b ,	PPv°,	PPc ^d ,	exp. ^a ,	PPv°,	PPc [₫] ,	exp. ^a ,	PPv ^c ,	PPc ^d ,
	T_0	T _e	T _e	T _e	$\Delta G_{1/2}$	ω_{e}	$\omega_{ m e}$	B ₀	B _e	B _e
2	0	0	0	0	824	837	828	3545	3519	3496
3	82	71	119	101	824	836	828	3570	3520	3496
1	813	857	913	923		838	823	3573 3568	3546	3543
2	912	918	1045	968	823	838	832	3622	3548	3539
0-	1679	1812	1396	1589		831	819	3579	3549	3614
1	1875	1937	1476	1679		828	838	3183 3614	3542	3620
0+	1925	1850	1715	1769		835	820	4003	3546	3607
4	2042	2084	2139	2302	822	838	828	3533	3518	3492
3	2143	2154	2286	2487	824	837	829	3566	3519	3495
3	2618	2726	2872	3086	828	841	833	3577	3550	3532
2	2771	2794	3039	3165	823	839	833	3602	3551	3532
2	3462	3453	3386	3771	821	836	834	3538	3554	3562
1	3635	3562	3391	3766	820	828	834	3656 3421	3552	3596
0-	3819	4176	3476	4120		836	843	3815	3559	3597
1	4134	4234	3605	4249		843	847	3524 3621	3541	3566
0+	4458	4217	4234	4314		837	843	3677	3558	3595

Table 24 Comparison of calculated and experimental spectroscopic constants for the states of the $4f^1\sigma^2\pi^4\sigma^1$ SC of CeO

^a Experimental data from Kaledin et al. (1993) and Linton et al. (1983b).

^b INDO/S-CI calculations from Kotzian and Rösch (1991b) and Kotzian et al. (1992).

° PP results with the 4f shell in valence space, from Dolg et al. (1991a).

^d PP results with the 4f shell in core space, from Dolg et al. (1993a).

formally arise from a \mathbb{R}^{2+} ion with one electron added to an empty or half-filled 4f shell and subsequently coupled to a $\sigma_{6s, 6p}$ orbital. The \mathbb{R}^{2+} ion is balanced by an O^{2-} counterion. CeO has the simplest electronic structure among these four molecules and has been studied by both ab initio PP SCF/CISD (Dolg et al. 1991a) and semiempirical INDO/S-CI (Kotzian and Rösch 1991b, Kotzian et al. 1992) calculations. In case of EuO and YbO the electronic structure is similar, but we have a hole in a half-filled (4f⁶) or filled (4f¹³) 4f shell instead. It was suggested however (Field 1982), that for EuO and YbO these are only low-lying SCs whereas the ground state arises from a half-filled (4f⁷) or filled (4f¹⁴) 4f shell and the $\sigma_{6s, 6p}$ orbital remains empty. The calculation of the energy separation between the states of these two SCs is a difficult challenge especially for ab initio methods, cf. e.g. the PP SCF/MRCI studies (Dolg et al. 1990b, 1992c). Some results of the INDO method for these critical cases are reported by Kotzian (1991).

The spectroscopic constants calculated for the 16 Ω levels of the 4f¹ $\sigma^2 \pi^4 \sigma^1$ SC of CeO derived from INDO/S-CI (Kotzian and Rösch 1991b, Kotzian et al. 1992) as well as PP SCF/CISD/CIPSO calculations (Dolg et al. 1991a) are summarized in table 24. According

	eight 122 coupled states to the sixteen 22 levels of the 41 ° 1 ° 1 ° 50 of CeO												
Ω				P	Pa				INDO/S-CI				
	³ Φ	$^{1}\Phi$	3Δ	$^{1}\Delta$	3П	-Π	3Σ	1Σ	configuration ^b				
2	92	0	5	3	0	0	0	0	91 φ σ				
3	51	40	9	0	0	0	0	0	90 φσ				
1	0	0	82	0	12	6	0	0	84 δσ				
2	0	0	46	34	20	0	0	0	82 δσ 17 πσ				
0-	0	0	0	0	59	0	41	0	73 πσ 25 σσ				
1	0	0	1	0	28	27	44	0	70 πσ 27 σσ				
0+	0	0	0	0	78	0	0	22	75 πσ 22 σσ				
4	100	0	0	0	0	0	0	0	99 φσ				
3	47	52	1	0	0	0	0	0	98 φ σ				
3	2	8	90	0	0	0	0	0	84 δσ				
2	8	0	46	41	5	0	0	0	84 δσ				
2	0	0	3	22	75	0	0	0	80 πσ 17 δσ				
1	0	0	13	0	59	11	17	0	81 πσ 14 δσ				
0-	0	0	0	0	41	0	59	0	72 σσ 25 πσ				
1	0	0	4	0	1	56	39	0	68 σσ 29 πσ				
0+	0	0	0	0	22	0	0	78	70 σσ 23 πσ				

Table 25

Comparison of quasirelativistic pseudopotential CI results and INDO/S-CI values for the contributions of the eight $\Lambda\Sigma$ coupled states to the sixteen Ω levels of the 4f¹ $\sigma^2\pi^4\sigma^1$ SC of CeO

^a Quasirelativistic pseudopotential CI results from Dolg et al. (1991a).

^b INDO/S-CI values from Kotzian and Rösch (1991b) and Kotzian et al. (1992).

to the SC model of Field (1982) a LFT calculation for the lanthanide 4f shell would be sufficient, whereas the σ , π and δ valence orbitals of a linear lanthanide molecule have to be treated by molecular orbital theory. A combination of the PP scheme that includes the 4f shell in the PP core with LFT calculations to obtain information on individual electronic states belonging to the SC under investigation has been developed (Dolg et al. 1993a). The results of such calculations for CeO are also included in table 24. The average error for the term energies of the 15 excited states is 128 cm⁻¹ for INDO/S-CI, 257 cm⁻¹ and 243 cm⁻¹ for the PP results with the 4f shell in the valence and core space, respectively. The corresponding errors of the LFT calculations of Dulick et al. (1986) and Carette and Hocquet (1988) are 84 cm⁻¹ and 282 cm⁻¹, respectively. We note that the accuracy of all these calculations is comparable to that of the best atomic calculations available for lanthanide ions, e.g. 222 cm⁻¹ for the term energies of Pr^{3+} 4f² from CCSD (coupled-cluster expansion with single and double substitutions) calculations (Eliav et al. 1995). According to the new experimental study of Kaledin et al. (1993) several states are affected by perturbations which might limit the validity of the SC model. The contributions of $\Lambda\Sigma$ states to the Ω levels are listed in table 25. Usually a good agreement exists between INDO/S-CI and PP SCF/CISD/CIPSO results. Larger deviations are present for the $\Omega = 0^{-}$ and nearby $\Omega = 1$ levels.

vibration	Subjectional frequencies ω_e of the $4f^2\sigma^2\pi^4 X^8\Sigma^-$ ground state and the $4f^6\sigma^2\pi^4\sigma^1 A^8\Sigma^-$ excited state of EuO ^a											
State	Space ^b	$R_{\rm e}$ (Å)		D_{e} (eV)		Te	(eV)		(cm ⁻¹)			
		calc. ^c	exp.d	calc.°	exp. ^d	calc. ^c	exp. ^d	calc. ^c	exp. ^d			
X ⁸ Σ ⁻	v	1.919	1.890	3.92	4.96	0.00	0.00	702	672, 688			
					±0.10							
Avg. ^e	с	1.912		3.22		0.00		644				
Avg. ^f	с	1.953		3.19		0.00		676				
$A^8\Sigma^-$	v	1.814				0.04	0.60	853	(830)			
							± 0.13					
Avg.°	с	1.820				0.11		819				
Avg. ^f	с	1.864				0.63		842				

Table 26 n 1.º 1/

^a Data taken from Dolg et al. (1990b, 1993a).

^b v, 4f shell in valence space; c, 4f shell in core space.

[°] Results from guasirelativistic pseudopotential configuration interaction calculations including the Langhoff-Davidson size-consistency correction.

Eu (v): PP with 35 valence electrons, (12s11p9d8f)/[9s8p6d5f] basis;

Eu (c): PP with 10 or 11 valence electrons;

O: (9s6p1d)/[4s3p1d] basis.

^d Experimental values from Gabelnick et al. (1974), McDonald (1985), Dulick et al. (1986).

For R_e , an average value was calculated from the rotational constants of ¹⁵¹EuO and ¹⁵³EuO;

for D_{r} , the zero-point vibration energy has been added to the experimental dissociation energy D_{0} .

^e 4f occupation number n(4f) = 7 or 6, (7s6p5d4f)/[5s4p3d4f] basis.

^f 4f occupation number $n(4f) \ge 7$ or 6, (7s6p5d2f)/[5s4p3d2f] basis.

The electronic structure of CeO may be compared to that of ThO. The latter molecule was studied in large-scale ab initio PP SCF/MRCI calculations by Marian et al. (1988) and recently by Küchle et al. (1994). The latter study also included spin-orbit CI results. The $\Omega = 0^+$ ground state is to 99.5% a ${}^1\Sigma^+$ state corresponding formally to a Th^{2+} 7s² O²⁻ closed shell configuration. The 5f orbitals participate considerably in chemical bonding, however in contrast to CeO no low-lying state arises from a configuration with an explicitly occupied 5f orbital. The charge distributions according to a Mulliken population analysis of the SCF ground-state wavefunctions, i.e. $Th^{0.77+}$ 5f^{0.38}6d^{1.02}7s^{1.73}7p^{0.10} O^{0.77-} 2s^{1.95}2p^{4.80} and Ce^{0.78+} 4f^{1.23}5d^{1.01}6s^{0.85}6p^{0.15} O^{0.78-} 2s^{1.91}2p^{4.87}, indicate a larger f covalency in ThO compared to CeO, whereas the d covalency is approximately equal in both cases. The charge distributions are formally related by a $f \rightarrow s$ electron rearrangement when going from CeO to ThO. This may be due to an increase in relativistic effects.

The low-lying electronic states arising from the $4f^7\sigma^2\pi^4$ and $4f^6\sigma^2\pi^4\sigma^1$ SCs of EuO have been investigated by Dolg et al. (1990b) using nonrelativistic and quasirelativistic energy-adjusted PPs which attribute the 4f shell either to the valence or to the core space. The two SCs correspond to SC II and SC I, respectively. PP SCF/CISD calculations with explicit treatment of the 4f shell have been performed for the $4f^7\sigma^2\pi^4$ $8\Sigma^-$

ground state and the $4f^6\sigma^2\pi^4\sigma^{1-8}\Sigma^-$ first excited state (table 26). At the highest level of approximation the derived theoretical spectroscopic constants for the ground state ($R_e = 1.919$ Å, $D_0 = 3.87$ eV, $\omega_e = 702$ cm⁻¹) are in good agreement with corresponding available experimental data ($R_e = 1.890$ Å, $D_0 = 4.92 \pm 0.10$ eV, $\omega_e = 672$ or 688 cm⁻¹) (Gabelnick et al. 1974, Dulick et al. 1986, McDonald 1985).

A more critical quantity seems to be the term energy of the first excited state. The different 4f occupations cause rather large differential relativistic and electron correlation effects. In order to judge the accuracy of the molecular calculations one may first consider a related excitation energy of the atom. The experimental atomic

$$4f^{7}6s^{2} {}^{8}S ({}^{8}S_{7/2}) \rightarrow 4f^{6}5d^{1}6s^{2} {}^{8}D ({}^{8}D_{3/2})$$

excitation energy may be estimated to be 3.64 eV (3.33 eV) with (without) averaging spinorbit splittings, although the term energy of the $({}^{8}D_{3/2})$ level has not yet been measured (Martin et al. 1978). Finite-difference all-electron calculations in the LS coupling scheme yield values of 6.01 eV and 2.35 eV at the nonrelativistic HF and quasirelativistic WB level, respectively. From these values the differential relativistic and correlation effects may be estimated as -3.66 eV and 1.29 eV when a simple additivity is assumed. The PP error of -0.01 eV and basis set error of 0.05 eV are negligible. Using the quasirelativistic PP in SCF/CISD calculations with (without) inclusion of one g function in the basis set one obtains values of 3.49 eV (3.29 eV), i.e., the remaining error is 0.15 eV. Spin-orbit effects were calculated to lower the excitation energy by 0.30 eV, which is essentially in agreement with the value of 0.31 eV estimated from experimental data. For the EuO molecule the best value for the excitation energy derived from $\Lambda\Sigma$ -coupled CISD calculations with (without) inclusion of one g function on Eu is 0.17 eV (0.04 eV). Spinorbit coupling mixes the excited states of the $4f^6\sigma^2\pi^4\sigma^1$ SC considerably (table 27) and lowers the excitation energy by 0.27 eV. The resulting values of -0.10 eV (-0.23 eV) are in poor agreement with the experimental result of $0.60\pm0.13\,\text{eV}$ from thermochemistry (Dulick et al. 1986). The remaining errors in the calculations are at least a factor of three larger than for the atom. Corresponding LFT studies yield a value of 0.41 eV (Dulick et al. 1986) or even 0.98 eV (Carette and Hocquet 1988).

The large relativistic and correlation effects may be qualitatively explained when looking at the Mulliken population analysis of the SCF wavefunction of the two states, i.e.

Eu^{1.04+} 4f^{7.04}5d^{$$0.84$$}6s ^{0.04} 6p ^{0.04} O^{1.04-} 2s ^{1.90} 2p ^{5.14} and
Eu ^{$0.83+$} 4f ^{6.145} d ^{1.056} s ^{0.836} p ^{0.15} O ^{$0.83-$} 2s ^{1.902} p ^{4.93} .

In the ground state 99.3% of the seven unpaired electrons are in Eu 4f orbitals. In the excited state 99.7% of six unpaired electrons are in Eu 4f orbitals, whereas the seventh unpaired electron is found to 98% on Eu, mainly in a 6s orbital (s 80.6%, p 14.4%, d 3.0%, f 0.0%). Therefore the exitation has $4f \rightarrow 6s$ character and the lower state is more stabilized by correlation effects, whereas the upper state is favoured by relativistic effects.

	obtained from DGCI calculations ^a											
No.	Ω	DGCI ^b	LFT°	8Σ	6Σ	8П	бП	⁸ Δ	6Δ	⁸ Φ	6Ф	
1	$\frac{1}{2}$	0	0	48	0	43	0	7	0	0	0	
2	32	165	199	49	0	43	0	6	0	0	0	
3	52	561	653	54	0	41	0	3	0	0	0	
4	$\frac{7}{2}$	1374	1481	70	0	25	0	3	0	0	0	
5	$\frac{1}{2}$	1470	1779	0	13	38	8	33	0	8	0	
6	3 2	1663	1966	1	9	45	5	36	0	2	0	
7	12	1999	2264	0	40	10	34	8	6	2	0	
8	52	2183	2359	0	7	74	0	15	0	2	0	
9	3 2	2331	2643	0	46	9	34	5	4	0	0	
10	$\frac{1}{2}$	2411	3129	12	0	3	2	39	0	42	0	
11	<u>3</u> 2	2725	3223	16	0	4	3	63	0	12	0	
12	$\frac{1}{2}$	3118	4014	4	0	20	0	8	2	65	0	
÷	÷	:		÷	÷	÷	÷	÷	:	÷	:	
49	$\frac{11}{2}$	10122		0	0	0	0	0	0	0	100	

Table 27

Comparison of DGCI and LFT relative term energies (cm⁻¹) for the low-lying states of the $4f^6\sigma^2\pi^4\sigma^1$ superconfiguration of EuO, and contributions ($\geq 1\%$) of the lowest AS-coupled states to $\omega\omega$ -coupled states obtained from DGCI calculations⁴

^a From Dolg et al. (1990b).

^b DGCI (double group configuration interaction) calculations.

^c LFT (ligand field theory) results from Dulick et al. (1986).

The problems associated with the 4f shell may be circumvented by including the 4f orbitals in the PP core and using the experimental atomic excitation energy of Eu to fix the potential curves in the separated atom limit. With this procedure a molecular excitation energy of 0.46 eV is obtained when spin-orbit corrections are included.

The QR-DFT calculations of Wang et al. (1995) yield for the EuO 4f⁷ $\sigma^2 \pi^4 \, ^8\Sigma^-$ groundstate spectroscopic constants ($R_e = 1.89 \, \text{\AA}$, $D_e = 5.19 \, \text{eV}$, $\omega_e = 675 \, \text{cm}^{-1}$) in good agreement with experimental data ($R_e = 1.89 \, \text{\AA}$, $D_e = 4.92 \, \text{eV}$, $\omega_e = 672 \, \text{cm}^{-1}$). The Mulliken charge distribution Eu^{0.72+} 4f^{7.04}5d^{0.96}6s^{0.21}6p^{0.13} O^{0.72-} 2s^{1.91}2p^{4.75} again shows a lower ionicity than derived from the PP SCF/CISD calculations. The calculated term energy of the excited 4f⁶ $\sigma^2 \pi^4 \sigma^1$ state is too high by more than 1 eV (2 eV) with (without) empirical correction for neglected correlation errors.

The situation encountered for YbO is even more complicated than for EuO, since the excitation from the supposed $4f^{14}\sigma^2\pi^{4-1}\Sigma^+$ (0⁺) ground state (Field 1982) to the $4f^{13}\sigma^2\pi^4\sigma^{1-3}\Sigma^+$ (0⁻) excited state now also involves the break-up of one electron pair. The SCs correspond to SC II and SC I, respectively. In early experimental work of Linton et al. (1983a) the configurational assignment of the $\Omega = 0$ ground state to the SC II was only tentative and based primarily on the similarity of the vibrational constant to that of EuO. Only two electronic states at term energies of 910 cm⁻¹ and 1010 cm⁻¹ were observed in low-resolution work. It was not possible to assign Ω values for them (possible values were 0, 1 or 2) or to link them to the SC I. The energy separation was found to be $0.05\pm0.22 \text{ eV}$ from thermochemistry (Dulick et al. 1986). LFT calculations gave 0.08 eV (Dulick et al. 1986) and 0.11 eV (Carette and Hocquet 1988). This was in disagreement with PP SCF/CISD calculations that attributed the Yb 4f shell to the core and gave a value of -0.77 eV (Dolg and Stoll 1989). It was suggested in this work that the YbO ground state might arise from the SC I instead of the SC II. This assignment was also supported by the relatively short experimental bond length of YbO ($R_e = 1.807 \text{ Å}$, Linton et al. 1983a) which is rather close to that observed for LuO ($R_e = 1.790 \text{ Å}$, Bernard and Effantin 1986), which has beyond any doubt a $4f^{14}\sigma^2\pi^4\sigma^{1-2}\Sigma^+$ ground state. However, the vibrational constant ($\Delta G_{1/2} = 683 \text{ cm}^{-1}$, Linton et al. 1983a) is very close to the corresponding values for EuO ($\omega_e = 672$ or 688 cm^{-1} , Gabelnick et al. 1974, McDonald 1985) and supports the original configurational assignment of the ground state by Field (1982) and Linton et al. (1983a).

This discrepancy between experiment and theory triggered further experimental (McDonald et al. 1990) and theoretical (Dolg et al. 1992c) studies on YbO which can only briefly be summarized here. McDonald et al. reported five excited states with term energies of 910, 1015, 2408, 2702 and 4287 cm⁻¹ above the $\Omega = 0^+$ ground state. The Ω values 0⁻, 1, 2, 1 and 3 were assigned. Since for three of them $\Delta G_{1/2} \approx 820-830 \text{ cm}^{-1}$ was measured they were assigned to the SC I. Another $\Omega = 0^+$ state with $\Delta G_{1/2} = 814 \text{ cm}^{-1}$ was found at 4637 cm⁻¹ but did not fit the energy level diagram derived from LFT calculations. The experimentally measured energy separation of 910 cm⁻¹ between the $\Omega = 0^+$ and $\Omega = 0^-$ states is the first definite linkage between the two SCs.

The Mulliken population analysis of the SCF wavefunctions of the $^1\Sigma^+$ and $^3\Sigma^+$ states yields

From these data one may conclude that the situation in YbO is similar to that for EuO, i.e. the molecular excitation has mainly $4f \rightarrow 6s$ character. The related atomic excitation energies have been discussed previously in sect. 3.1. The errors in the uncorrelated atomic studies amounted to up to 0.5 eV and were all favouring the SC with the higher 4f occupation number. They were approximately compensated by neglected electron correlation effects. The theoretical spectroscopic constants of the presumable ${}^{1}\Sigma^{+}$ ground state ($R_{e} = 1.886$ Å, $D_{e} = 2.53$ eV, $\omega_{e} = 679$ cm⁻¹) were found to be only in very modest agreement with the corresponding experimental values ($R_{e} = 1.807$ Å, $D_{e} = 4.11-4.33$ eV, $\omega_{e} = 699$ cm⁻¹) (Yokozeki and Menzinger 1976, Cosmovici et al. 1977, Murad and Hildenbrand 1980, Linton et al. 1983a, Dulick et al. 1986) although 4 g functions as well as 2 d and 1 f functions have been included in the Yb and O basis sets, respectively (table 28). Much better results have been obtained at the same level of theory for YbH (sect. 3.2.1) and YbF (sect. 3.2.3). The term energy of the ${}^{3}\Sigma^{+}$ was calculated to be -0.52 eV in harsh disagreement with the (theoretically) spin-orbit corrected experimental value of 0.61 eV. After correcting for spin-orbit effects the $\Omega = 0^{-}$ state is found to be

 ${}^{3}\Sigma^{+}$

•	and vibration	onal freque	ncies ω_e of	the 4f ¹⁴ o ²	$^{2}\pi^{4}$ $^{1}\Sigma^{+}$ and	$4f^{13}\sigma^2\pi^4\sigma$	$^{1}\Sigma^{+}$ states	of YbO ^a	67 6
State	Space ^b	R _e	(Å)	$D_{\rm e}~({\rm eV})$ $T_{\rm e}~({\rm eV})$				$\omega_{\rm c}~({\rm cm}^{-1})$	
	-	calc. ^c	exp. ^d	calc. ^c	exp.d	calc. ^c	exp. d	calc. ^c	exp.d
¹ Σ ⁺	v	1.886	1.807	2.53	4.11– 4.33	0.00	0.00	679	699
	c	1.938		2.48	≼3.87	0.00		602	

-0.52

0.13

0.61

907

851

Table 28

Comparison of calculated and experimental results for the bond lengths R_e , binding or term energies D_e , T_e

^a Data taken from Dolg et al. (1992c).

v с

^b v, 4f shell in valence space; c, 4f shell in core space.

1.768

1.802

^e Results from quasirelativistic pseudopotential multi-reference configuration interaction calculations including the Langhoff-Davidson size-consistency correction.

Yb (v): PP with 42 valence electrons, (12s11p9d8f4g)/[9s8p6d5f4g] basis;

Yb (c): PP with 10 or 11 valence electrons, (7s6p5d2f)/[5s4p3d2f] basis;

O: (9s6p1d)/[4s3p1d] basis.

^d Experimental values from Yokozeki and Menzinger (1976), Cosmovici et al. (1977), Murad and Hildenbrand (1980), Linton et al. (1983a), Dulick et al. (1986).

For D_e , the zero-point vibration energy has been added to the experimental dissociation energy D_0 .

0.93 eV lower in energy than the $\Omega = 0^+$ state (table 29), i.e. the remaining error with respect to experiment is 1.04 eV. Corresponding PP SCF/CISD calculations that include the 4f shell in the core in combination with LFT theory find the $\Omega = 0^{-1}$ state 0.35 eV lower than the $\Omega = 0^+$ state, i.e. the remaining error is 0.46 eV. Similar to the calculations that explicitly treat the 4f shell the theoretical spectroscopic constants are only in poor agreement with experimental data.

The contributions of the $\Lambda\Sigma$ states to the sixteen Ω levels of the 4f¹³ $\sigma^2\pi^4\sigma^1$ SC of YbO are listed in table 30. It is obvious that it is necessary to include spin-orbit interaction in order to get a reliable description of these states. Dolg et al. (1992c) also investigated the consequences of an avoided crossing of the two lowest $\Omega = 0^+$ states belonging to the two SCs. It was found that for a downward shift of the potential curve of SC II with respect to SC I of about 0.70 eV (this might account for neglected electron correlation effects), the lowest $\Omega = 0^+$ state has $\Delta G_{1/2} = 734 \text{ cm}^{-1}$ and $B_e = 0.3560 \text{ cm}^{-1}$ in reasonable agreement with the experimental values of $\Delta G_{1/2} = 683 \text{ cm}^{-1}$ and $B_e = 0.3502 \text{ cm}^{-1}$. Although the vibrational frequency seems to be diagnostic for a ground state arising from SC II, the ground state actually has to 97.7% the character of SC I. It is suggested that such an avoided crossing might limit the diagnostic value of $\Delta G_{1/2}$ or B_e for a configurational assignment of the state under consideration. In addition we note that the SC concept is not able to deal with such complicated situations. Therefore, the electronic structure of YbO still seems to be an open problem and a challenge for future more accurate investigations.

	1		F	1	SC of	YbO				
Ω		Term energ	gies (cm ⁻¹))	Vibrati	Vibrational const. (cm ⁻¹)			al const. (1	$0^{-4} \mathrm{cm}^{-1}$
	$\overline{\begin{array}{c} \text{exp.}^{a}, \\ T_{0} \end{array}}$	INDO ^b , T_e	PPv°, T _e	PPc ^d , T _e	$\frac{\exp^{a}}{\Delta G_{1/2}}$	PPv°, ω _e	PPc ^d , ω _c	$exp.^{a}, B_{0}$	PPv ^c , B _c	PPc ^d , B _e
0+	0	31073	8410	5510	683	686	687	3524	3212	3212
0-	910	910°	910°	910°		884	859		3592	3572
1	1015	963	1029	1011	824	880	859		3588	3572
0+		1014	1313	1192		884	859		3592	3572
2	2408	2317	1885	1784	821	883	856		3569	3553
1	2702	2432	2125	1896		871	856		3569	3557
3	4287	3048	3310	3104	830	881	850		3561	3525
2		3113	3456	3285		882	850		3561	3525
4		3388	3806	4787		875	841		3569	3490
3		3504	3900	5062		876	842		3569	3494
0-		10565	11208	11358		885	859		3588	3569
1		10684	11424	11602		876	858		3584	3569
0+		10570	11489	11818		886	859		3580	3569
1		12221	12992	12959		880	853		3561	3537
2		12242	13072	13083		883	853		3565	3537
2		12851	13878	14980		877	843		3569	3498
3		12944	13982	15297		877	843		3569	3498

Table 29 Comparison of calculated and experimental spectroscopic constants for the states of the $4f^{13}\sigma^2\pi^4\sigma^1$ and $4f^{14}\sigma^2\pi^4$

^a Experimental data from McDonald et al. (1990).

^b INDO/S-CI calculations from Kotzian (1991).

^c PP results with the 4f shell in valence space, from Dolg et al. (1992c).

^d PP results with the 4f shell in core space, from Dolg et al. (1992c).

^e The theoretical T_e values for the lowest $\Omega = 0^-$ state have been shifted to agree with the experimental result 910 cm⁻¹.

The QR-DFT calculations of Wang et al. (1995) find a 0⁺ ground state that is a mixture of $\frac{2}{3}$ Yb²⁺(4f¹⁴)O²⁻ and $\frac{1}{3}$ Yb²⁺(4f¹³6s¹)O²⁻. Except for the bond length the calculated parameters ($R_e = 1.90$ Å, $D_e = 4.13$ eV, $\omega_e = 680$ cm⁻¹) are in satisfactory agreement with experimental data ($R_e = 1.807$ Å, $D_e = 4.11-4.33$ eV, $\omega_e = 699$ cm⁻¹). Wang et al. find the $4f_{5/2}^6 4f_{7/2}^7 \sigma^2 \pi^4 \sigma^1$ average only 0.6 eV above $4f^{14}\sigma^2 \pi^4$. The reader is reminded that the corresponding energy difference for EuO turned out to be too high by about 1 eV even after empirical corrections. If a similar error occurs for YbO, $4f^{13}\sigma^2\pi^4\sigma^1$ might well fall by about 0.4 eV below $4f^{14}\sigma^2\pi^4$. This would be consistent with the findings from the PP studies discussed above. The Mulliken charge distributions (Yb^{0.62+} $4f^{13.86}5d^{1.01}6s^{0.31}6p^{0.20}$ O^{0.62-} $2s^{1.92}2p^{4.70}$ and Yb^{0.66+} $4f^{13.02}5d^{1.28}6s^{0.90}6p^{0.14}$ O^{0.66-} $2s^{1.92}2p^{4.74}$) again indicate a lower ionicity when compared to the PP results.
676

		U	,						
Ω				Р	P ^a				INDO/S-CI configuration ^b
	3Σ	1Σ	3П	п'	³ Δ	$^{1}\Delta$	³ Φ	۱Φ	
0-	69	0	39	0	0	0	0	0	63 σ ⁻¹ σ 36 π ⁻¹ σ
1	60	0	29	10	0	0	0	0	64 σ ⁻¹ σ 36 π ⁻¹ σ
0+	0	58	42	0	0	0	0	0	67 σ ⁻¹ σ 33 π ⁻¹ σ
2	0	0	78	0	13	8	0	0	75 π ⁻¹ σ 4 δ ⁻¹ σ
1	2	0	30	45	23	0	0	0	74 π ⁻¹ σ 26 δ ⁻¹ σ
3	0	0	0	0	87	0	9	4	86 δ ⁻¹ σ 14 φ ⁻¹ σ
2	0	0	0	0	42	44	13	0	86 δ ⁻¹ σ 13 φ ⁻¹ σ
4	0	0	0	0	0	0	0	100	100 φ ⁻¹ σ
3	0	0	0	0	0	0	48	51	99 φ ⁻¹ σ
0-	39	0	61	0	0	0	0	0	33 σ ⁻¹ σ 66 π ⁻¹ σ
1	37	0	32	30	1	0	0	0	36 σ ⁻¹ σ 64 π ⁻¹ σ
0+	0	42	58	0	0	0	0	0	33 σ ⁻¹ σ 66 π ⁻¹ σ
1	0	0	8	15	76	0	0	0	27 π ⁻¹ σ 73 δ ⁻¹ σ
2	0	0	21	0	40	38	1	0	24 π ⁻¹ σ 75 δ ⁻¹ σ
2	0	0	0	0	4	10	86	0	14 δ ⁻¹ σ 86 φ ⁻¹ σ
3	0	0	0	0	13	0	43	45	13 δ ⁻¹ σ 86 φ ⁻¹ σ

Table 30 Comparison of quasirelativistic pseudopotential CI results and INDO/S-CI values for the contributions of the eight $\Lambda\Sigma$ coupled states to the sixteen Ω levels of the 4f¹³ $\sigma^2\pi^4\sigma^1$ SC of YbO

^a Quasirelativistic pseudopotential CI results from Dolg et al. (1992c).

^b INDO/S-CI values from Kotzian (1991).

INDO/S-CI results for EuO and YbO are available (Kotzian 1991), but have not been published. For EuO the SC II is calculated 3200 cm^{-1} lower in energy than SC I, whereas for YbO it was found to be 30200 cm^{-1} higher in energy.

The molecules PrO and TmO have been studied by Kotzian and Rösch (1991a) using their INDO/S-CI method. The ground states arise from SC I. Formally a R²⁺ ion with two electrons (4f²) or two holes (4f¹²) in the 4f shell is coupled to a singly occupied $\sigma_{6s, 6p}$ orbital which is polarized away from the O²⁻ counterion. Other SCs were calculated to be at least one electron volt higher in energy. For PrO the agreement between INDO/S-CI term energies and experimental values (Dulick et al. 1981, Dulick and Field 1985) as well as ligand field theoretical results (Dulick et al. 1986, Carette and Hocquet 1988) is good, i.e. the experimentally observed $\Omega = 3.5$ ground state is found by all theoretical calculations and maximum deviations between the term energies are at most a few 100 cm⁻¹. No experimental energy-level diagram is available for TmO. The INDO/S-CI calculations predict a $\Omega = 3.5$ ground state, whereas the ligand field studies (Dulick et al. 1986, Carette and Hocquet 1988) find $\Omega = 0.5$. The maximum deviations between the INDO/S-CI and LFT term energies are increased to a few 1000 cm⁻¹. Further experimental as well as theoretical studies are required to clarify the situation.

3.2.3. Monofluorides

The ground state configurations of the lanthanide monofluorides may be assumed to arise from either of the two superconfigurations (SC):

I [R 4f^{*n*}]
$$\sigma_{F2p}^2 \pi_{F2p}^4 \sigma_{R6s,6p}^2$$
 or II [R 4f^{*n*+1}] $\sigma_{F2p}^2 \pi_{F2p}^4 \sigma_{R6s,6p}^1$

SCF/CISD results for the spectroscopic constants of the lanthanide monofluorides in these SCs have been obtained with PPs that treat the 4f shell as part of the core (Dolg 1989, 1995, Dolg and Stoll 1989, Dolg et al. 1989c). The CISD values are compared to experimental data in table 31. Improved results for CeF and YbF from calculations that combine the PP approach for the valence subconfiguration with LFT for the open 4f shell are also available (Dolg et al. 1992b, 1993a). Using the best results for LaF and LuF as well as EuF and YbF as basis for a linear interpolation the binding energies displayed in fig. 10 are obtained. The ground states of the monofluorides may be predicted to arise from SC I for LaF-NdF, GdF-TmF and LuF as well as from SC II for PmF-EuF and YbF. The trend of these binding energies is in reasonable agreement with the available experimental values. Gotkis (1991) used a simple electronic structure model based on experimental data to explain the ground-state configuration of the lanthanide monohalides and their cations. According to his findings the lanthanide monofluorides belong to the following two structural groups: those with a R^+ 4fⁿ6s² cation (LaF, GdF-TmF, LuF) and those with a R^+ 4fⁿ⁺¹6s¹ cation (PrF-EuF, YbF) bound to the F⁻ anion. This would roughly agree with the predictions from the PP SCF/CISD calculations when the binding energies of the SC II are shifted by about 0.5 eV. In addition, Gotkis claims that for CeF probably a Ce⁺ $4f^{1}5d^{1}6s^{1}$ cation is appropriate. Using his model he also explained the nonmonotonic trend in the molecular ionization energies. The ground states of the cations should arise from $R^{2+} 4f^n 6s^1$, $R^{2+} 4f^n 5d^1$ or $R^{2+} 4f^{n+1}$ cations as well as a F⁻ anion. According to his findings TbF, HoF and ErF rearrange their core structure from $4f^n$ to $4f^{n+1}$ upon ionization, whereas the other molecules keep their 4f occupation unchanged. For the discussion of the other halides we refer to the original paper. Finally, we want to add here that we disagree with the comment of Gotkis (1991) that "in case of lanthanide compounds, present quantum calculations are largely empirical, and their results are predetermined to a large extent by a subjective idea adopted at the outset of the computation". These comments are certainly much more appropriate for a strict jonic model based on pure atomic configurations as advocated by Gotkis. Unfortunately Gotkis did not cite a single quantum-chemical calculation available in 1991 in order to prove his statement.

Dolg et al. (1992b) investigated YbF using a Yb⁴²⁺ [Ar 3d¹⁰] core PP for Yb and large basis sets including up to four g functions on Yb. The results of these PP SCF/MRCI calculations in the AS coupling scheme are summarized in table 32. The spectroscopic constants of the X ${}^{2}\Sigma^{+}$ ground state are in excellent agreement with the experimental values. Spin-orbit interaction was also included by means of the Columbus DGCI code (A.H.H. Chang and Pitzer 1989). The $\Omega = \frac{1}{2}$ lowest excited state (58% ${}^{2}\Sigma^{+}$, $42\% {}^{2}\Pi$) of the 4f¹³ $\sigma^{2}\pi^{4}\sigma^{2}$ SC is located 6099 cm⁻¹ above the 4f¹⁴ $\sigma^{2}\pi^{4}\sigma^{1}$ X ${}^{2}\Sigma^{+}$ $\Omega = \frac{1}{2}$

m 11	1 1
Table	- 11
rabie	J I

Binding energies D_e , bond lengths R_e , vibrational frequencies ω_e and dipole moments μ_e for the lanthanide monofluorides from configuration interaction calculations including the Langhoff–Davidson size-consistency correction in comparison with experimental data^a

Molecule	n(4f) ^b	Method ^c	De	(eV)	$R_{\rm e}$ ((Å)	ω, (cm ⁻¹)	$\mu_{\rm e}$ (D)
			calc.	exp.d	calc.	exp.d	calc.	exp. ^d	calc.
LaF	0	a, c	5.45	6.23	2.181	2.027	528	570	3.19
		b, c	5.77		2.183		543		3.14
		b, d	6.02		2.118		571		2.07
	$\geqslant 0$	b, e	6.55		2.022		582		1.11
CeF	1	a, c	5.48		2.159		532		3.13
PrF	2	a, c	4.95		2.145		535		3.11
	3	a, c	4.99		2.252		488		3.47
NdF	4	a, c	4.98	5.90	2.242		493		3.47
PmF	5	a, c	4.94		2.229		496		3.51
SmF	6	a, c	4.91	5.49	2.216		498		3.51
EuF	7	a, c	4.89	5.45	2.206		502		3.50
		b, c	4.51		2.208		429		4.22
		b, d	5.02		2.138		472		3.31
	≥7	b, e	5.35		2.092		479		2.88
GdF	7	a, c	5.73	6.11	2.079		548		6.97
TbF	8	a, c	5.75		2.067	1.960	542	616	6.75
DyF	9	a, c	4.91	5.49	2.059		544		6.56
HoF	10	a, c	4.87	5.60	2.049	1.940	545	615	6.36
ErF	11	a, c	5.09	5.86	2.041		545		6.22
TmF	12	a, c	4.41		2.033		544		6.05
	13	a, c	4.72	5.28	2.148		520		3.69
YbF	14	a, c	4.67	4.83	2.146	2.016	516	502	3.72
		b, c	4.20		2.140		437		4.42
		b, d	4.70		2.067		478		3.56
		b, e	4.99		2.052		495		2.03
LuF	14	a, c	6.18	(5.93)	2.018	1.917	546	612	2.61
		b, c	6.76		2.007		532		2.95
		b, d	7.04		1.936		598		2.07
		b, e	7.28		1.930		599		3.45

^a Data from Dolg and Stoll (1989) and Dolg (1995).

^b n(4f), the 4f occupation number modeled by the lanthanide pseudopotential.

^c (a) nonrelativistic pseudopotential;

(b) quasirelativistic pseudopotential;

(c) basis sets: R (7s6p5d)/[5s4p3d], F (9s6p)/[4s3p];

(d) basis sets: R (7s6p5d2f)/[5s4p3d2f], F (9s6p2d)/[4s3p2d];

(e) basis sets: R (8s7p6d6f), F (13s7p4d3f2g).

^d Only a selection of the experimental data summarized by Dolg and Stoll (1989) has been reproduced; the binding energies D_e have been derived from the dissociation energies D_0 by adding an estimate for the zero-point vibration energy (0.03 eV).



Fig. 10. Binding energies for the low-lying superconfigurations (SC) (I, $4f^{n}\sigma^{2}\pi^{4}\sigma^{2}$; II, $4f^{n+1}\sigma^{2}\pi^{4}\sigma^{1}$) of the lanthanide monofluorides. Extrapolated theoretical values for pseudopotential configuration interaction calculations based on the b, e entries in table 31.

State	Method	Basis ^b	$R_{\rm e}$ (Å)	$D_{\rm e}$ (eV)	$\omega_{e} \ (cm^{-1})$	μ_{e} (D)
X ² Σ ⁺	MRCI (SCF)	0g	2.043 (2.067)	5.00 (4.00)	504 (492)	3.40 (3.60)
		4g	2.045 (2.071)	4.90 (3.91)	492 (481)	3.55 (3.73)
	exp. ^c		2.016	4.83-4.89	502	
$A^{2}\Sigma^{+}$	MRCI (SCF)	0g	1.927 (1.941)	4.56 (5.25)	652 (619)	1.65 (1.84)
		4g	1.917 (1.941)	3.62 (5.22)	639 (611)	1.71 (1.89)

Table 32Molecular constants for the $4f^{14}\sigma^2\pi^4\sigma^1 X^2\Sigma^+$ ground state and the $4f^{13}\sigma^2\pi^4\sigma^2 A^2\Sigma^+$ excited state of YbF^a

^a From Dolg et al. (1992b).

^b Yb: (12s11p9d8f)/[9s8p6d5f] augmented with *n* g functions, quasirelativistic Yb⁴²⁺ [Ar 3d¹⁰] core PP; H: (9s6p1d)/[4s3p1d].

^c Experimental data taken from Huber and Herzberg (1979), Barrow and Chojinicki (1975), Yokozeki and Menzinger (1976).

ground state, when the best AS-coupled MRCI results were corrected for spin-orbit effects derived from DGCI calculations. We note that the correlation contribution to this energy separation is 0.69 eV and 1.60 eV without and with g functions on Yb, respectively. Moreover, without any correlation effects the ground state would be predicted to arise from the $4f^{13}\sigma^2\sigma^2$ SC. For a discussion of higher excited states we refer to the original paper. From ESR spectroscopy Van Zee et al. (1978) deduced that bonding in YbF is

Molecule	D_{e}	(eV)	R _e	(Å)	ω_{e} (e	cm ⁻¹)	$\mu_{\rm e}$ (D)	
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	
LaF	6.38	6.23	2.07	2.027	594	570	2.18	
GdF	5.85	6.11	1.96		613		1.18	
YbF	5.18	4.83	2.07	2.016	489	502	3.64	
LuF	7.26	(5.93)	1.95	1.917	586	612	2.11	

Table 33

Binding energies D_e , bond lengths R_e , vibrational frequencies ω_e and dipole moments μ_e for the ground states of selected lanthanide monofluorides from relativistically corrected density-functional studies in comparison with experimental data^a

^a Calculations from Wang and Schwarz (1995).

Only a selection of the experimental data summarized by Dolg and Stoll (1989) has been reproduced; the binding energies D_e have been derived from the dissociation energies D_0 by adding an estimate for the zero-point vibration energy.

essentially that of an ion pair Yb⁺F⁻ and only 2% of the spin density is on F. It was deduced that 80% of the unpaired electron density is in the Yb 6s orbital. This agrees quite well with the results of a SCF Mulliken population analysis, where 99% of the unpaired electron is assigned to Yb (Yb s 84%, p 15%, F p 1%). The singly occupied orbital is strongly polarized away from F and contributes with -4.4 D to the total SCF dipole moment of 3.7 D. The doubly occupied bonding σ orbital is localized on F (Yb s 1%, p 1%, d 3%, F s 95%).

Shortly before this article was completed a relativistically corrected density-functional (Snijders and Baerends 1978, Snijders et al. 1979) study of selected lanthanide monofluorides became available (Wang and Schwarz 1995). The results for the ground states obtained with a gradient correction for the exchange potential (Becke 1988) as well as correlation contributions due to Vosko et al. (1980) with self-interaction correction according to Stoll et al. (1978, 1980) are listed in table 33. For YbF the results ($R_e = 2.07$ Å, $D_e = 5.18$ eV, $\omega_e = 489$ cm⁻¹) are in good agreement with the best PP CI results ($R_e = 2.045$ Å, $D_e = 4.90$ eV, $\omega_e = 492$ cm⁻¹) and available experimental data ($R_e = 2.016$ Å, $D_e = 4.83-4.89$ eV, $\omega_e = 502$ cm⁻¹).

3.2.4. *Dimers*

Van Zee et al. (1994) investigated the Gd₂ dimer with ESR spectroscopy and found a total spin of S=9, i.e. 18 unpaired spins are ferromagnetically coupled. The ground state was assigned to be a ¹⁹ Σ state. The authors suggest that Gd₂ might be the diatomic molecule with the highest spin multiplicity. These experimental findings are essentially in agreement with the results of earlier PP SCF/CISD calculations that include a 4f⁷ subconfiguration into the Gd PP core (Dolg et al. 1992a). In these studies a [4f⁷][4f⁷] $\sigma_g^2 \sigma_u^1 \sigma_g^1 \pi_u^2$ ground-state superconfiguration was predicted. In view of the large energy difference of more than 30 000 cm⁻¹ between the Gd³⁺ 4f⁷ 8S_{7/2}

ground state and the first excited state it seems to be likely that the 7 unpaired spins within each of the 4f shells are coupled to yield a high-spin $S = \frac{7}{2}$ state on each center. The valence substate was calculated to be a ${}^{5}\Sigma_{u}^{-}$ state, i.e., the 4 unpaired electrons in the valence orbitals are also coupled to yield a high-spin state. It is impossible, however, to predict the coupling between the two 4f shells and the valence shell with the superconfiguration-based PP approach, although the high-spin possibility seems to be plausible. Calculations which include the Gd 4f orbitals explicitly in the valence space and also account for spin-orbit interaction as well as electron correlation effects would be required for improved theoretical investigations on Gd₂. Although the calculation of the ferromagnetically coupled ${}^{19}\Sigma$ state is probably feasible, difficulties might arise for states with lower spin multiplicities due to the large number of determinants required to set up the zeroth-order wavefunction for a subsequent MRCI treatment.

Dolg et al. (1992a) used PPs for a fixed 4f occupation number, SCF/CISD/CEPA as well as SCF and subsequent correlation energy functional calculations to investigate the lowest superconfigurations of the homonuclear dimers R_2 . The study is limited by the fact that only SCs with equal 4f occupation on both metals could be considered. For La₂ a $(4f^0)(4f^0)\sigma_g^2\sigma_u^1\sigma_g^1\pi_u^2 {}^5\Sigma_u^-$ ground state (La $5d\sigma^{0.51}5d\pi^{0.88}6s\sigma^{1.41}6p\sigma^{0.08}6p\pi^{0.12})$ was found in agreement with experimental and theoretical evidence for the lighter homologues Sc₂ and Y₂. For Lu₂ all SC with significant contributions of $5d\pi$ orbitals were found to be rather high in energy probably due to a relativistic destabilization, and a $(4f^{14})(4f^{14})\sigma_g^2\sigma_u^2\sigma_g^2$ Σ_g^+ ground state (Lu $5d\sigma^{0.45}6s\sigma^{1.82}6p\sigma^{0.73}$) was obtained. Therefore, the experimentally observed rather large difference in the binding energies (La 2.52 ± 0.22 eV, Lu 1.43 ± 0.34 eV, Connor 1986) may be explained in terms of a double and a single bond for La₂ and Lu₂, respectively. Probably due to the lack of higher angular momentum basis functions and a multi-reference correlation treatment the calculated CISD results, i.e. 1.17 eV and 0.55 eV, are only in modest agreement with the experimental values. In contrast to these relatively strong bonds Eu_2 and Yb₂ have a $(4f^{n+1})(4f^{n+1})\sigma_g^2\sigma_u^2$ ground-state configuration (n=6, 13 for Eu, Yb) and form only a weak van der Waals bond. The ground state of Yb₂ may be assumed to be ${}^{1}\Sigma_{p}^{+}$, whereas for Eu₂ one might consider S=0-7, i.e. all possibilities between antiferromagnetic and ferromagnetic coupling of two 4f7 8S7/2 cores. In analogy to the ${}^{1}\Sigma_{g}^{+}$ ground state of the van der Waals dimer Mn₂ (Kirkwood et al. 1991) which arises from a $(3d^5)(3d^5)\sigma_g^2\sigma_u^2$ configuration, a ${}^1\Sigma_g^+$ ground state seems to be most likely.

The calculated CISD binding energies (Eu₂ 0.04 eV, Yb₂ 0.05 eV) are in reasonable agreement with the experimental values (Eu₂ $0.30\pm0.17 \text{ eV}$, Yb₂ $0.17\pm0.18 \text{ eV}$, Connor 1986). The binding energies of the lanthanide dimers calculated at the SCF level and using the correlation energy functionals of Perdew (1986) and Hu and Langreth (1985) are shown in fig. 11. The calculated bond lengths and vibrational constants of the dimers R₂ are predictions. The assignments for the ground state SCs should be regarded as preliminary.



Fig. 11. Binding energies of the homonuclear lanthanide dimers. HL and P denote SCF values corrected with correlation contributions calculated with the functionals of Hu and Langreth (1985) and Perdew (1986), respectively. Data taken from Dolg et al. (1992a).

3.2.5. Rare gas compounds

Quantum chemistry appears to be currently one of the best ways to study helium chemistry (Frenking and Cremer 1990), especially for neutral species like HeLiH (Kaufman and Sachs 1969) or HeBeO (Koch et al. 1986). A large number of stable or metastable charged species HeX^{n+} are known either from mass spectroscopy or from calculations (Hotokka et al. 1984, Koch et al. 1987, Frenking and Cremer 1990). Dolg et al. (1991c) investigated the triply charged molecular cations RHe^{3+} (R=La, Eu, Gd, Yb, Lu) using guasirelativistic PPs at the SCF, CEPA, CASSCF and MRCI level. The existence of these compounds has been suggested by Jørgensen (1988, 1989) and Jørgensen and Frenking (1990). The ground states arise from a R^{3+} 4fⁿ He 1s² SC (R=La, Gd, Lu) (Mulliken population $R^{2.98+}$ He^{0.02+}) or a R^{2+} 4fⁿ⁺¹ He⁺ 1s¹ SC (R=Eu, Yb) (Mulliken population $R^{2.00+}$ He^{1.00+}). This is due to the fact that for the first group of atoms the third ionization potential (IP₃ = 19.18 eV, La, 20.63 ± 0.10 eV, Gd, 20.96 eV, Lu, Martin et al. 1978) is significantly smaller than the first ionization potential of helium ($IP_1 = 24.59 \text{ eV}$, Moore 1949), whereas for the second group (IP₃ = $24.92 \pm 0.10 \text{ eV}$, Eu, $25.05 \pm 0.03 \text{ eV}$, Yb, Martin et al. 1978) it is somewhat larger. The La, Gd and Lu compounds have been found to be stable with respect to a decay in R³⁺ and He (binding energies 0.24 eV, 0.31 eV and 0.39 eV), whereas the molecules formed by Eu and Yb seem to be metastable (binding energies -0.03 eV and -0.08 eV) and may dissociate into R²⁺ and He⁺ (estimated barrier heights 0.30 eV and 0.38 eV).

3.2.6. Miscellaneous diatomics

The high bond stabilities in LaAu and LuAu have been studied by Schwerdtfeger and Dolg (1991) using relativistic as well as nonrelativistic ab initio PPs and correlation treatments like Møller–Plesset perturbation theory up to fourth order (MPn, n=2, 3, 4), configuration interaction with single and double substitutions (CISD) and coupled electron

Molecule	D_{e}^{b} (eV)		$R_{\rm e}$ (Å)		$\omega_{\rm e}~({\rm cm}^{-1})$		$\mu_{\rm e}$ (D)	
	CEPA ^c	MRCI ^c	CEPA ^c	MRCI°	CEPA°	MRCI ^c	CEPA °	MRCI°
LaAu	3.04	2.99	2.737	2.743	154	151	2.57	2.55
LuAu	3.66	3.47	2.635	2.632	148	149	2.56	1.68

Table 34 Binding energies D_e , bond lengths R_e , vibrational frequencies ω_e and dipole moments μ_e from CEPA-1 and MRCI pseudopotential calculations for the ${}^{1}\Sigma_{g}^{+}$ ground states of LaAu and LuAu^a

^a From Dolg 1995.

^b The experimental dissociation energies are 3.45 eV (LaAu) and 3.41 eV (LuAu) (Huber and Herzberg 1979).

^c CEPA, coupled electron-pair pseudopotential calculations;

MRCI, multi-reference configuration interaction pseudopotential calculations.

Relativistic pseudopotentials with 11 (La, Lu) and 19 (Au) valence electrons;

basis sets: La, Lu (8s7p6d6f1g), Au (9s8p7d5f1g).

pair approximations (CEPA-1/2). ${}^{1}\Sigma^{+}$ ground states have been assumed for both molecules and spin-orbit contributions have been estimated from the available experimental data for the separated atoms. Among the gaseous diatomic intermetallic group-11 (Cu, Ag, Au) compounds those containing gold have the highest binding energy, except for the series AuCu, AuAg and Au₂. The high stability of the metal-gold bond was empirically explained using the Pauling model,

$$D(A - B) = \frac{1}{2}[D(A_2) + D(B_2)] + Q[EN(A) - EN(B)]^2,$$
(55)

with the relativistic increase of the dissociation energy (D_0) of Au₂ (first term; Cu₂ 2.03 eV, Ag₂ 1.66 eV, Au₂ 2.30 eV) and of the electronegativity (EN) of Au (second term; Cu 1.9, Ag 2.1, Au 2.4). Among metal-gold diatomics, the lanthanide-gold compounds LaAu, CeAu and LuAu have the highest values. High relativistic contributions to binding energies are therefore expected for these molecules. Schwerdtfeger and Dolg obtained at the CEPA-1 level 56.7 kcal/mol and 71.4 kcal/mol for LaAu and LuAu, respectively. The relativistic contribution for LaAu is 28.7 kcal/mol (51%), that for LuAu even 48.8 kcal/mol (68%). The experimental dissociation energies are 80 ± 5 kcal/mol and 79 ± 4 kcal/mol (Huber and Herzberg 1979). The reason for the significant discrepancy for LaAu is due to the limited basis sets: recent CEPA-1 calculations using large uncontracted basis sets yield binding energies of 70.1 kcal/mol and 84.4 kcal/mol for LaAu and LuAu, respectively (table 34) (Dolg 1995). Interestingly the nonrelativistic value for the lanthanide contraction (0.169 Å) is higher than the relativistic value (0.117 Å). The relativistic bond-length contractions are 0.413 Å and 0.361 Å, respectively. The Mulliken charges on Au are very similar for both molecules, i.e. -0.80 (-0.41) for LaAu and -0.83 (-0.44) for LuAu from relativistic (nonrelativistic) SCF calculations, however the corresponding dipole moments +2.44 (+3.76) and +2.38 (+0.59) indicate a dramatic change in the molecular charge distribution due to relativistic effects (a positive sign of the dipole moment corresponds to $R^{\delta+}Au^{\delta-}$ polarity; unfortunately, in the original paper the signs of the LaAu dipole moments have been reversed).

3.3. Polyatomic molecules

3.3.1. Hydrides

The results of HF- and DHF-OCE calculations for the tetrahedral molecules CeH₄ and ThH₄ were compared by Pyykkö and Desclaux (1978). For both molecules small relativistic bond-length expansions were found. By comparison to HfH₄ and $_{104}$ EH₄ the values of the lanthanide and actinide contraction were established to be 0.19 Å and 0.30 Å, respectively (cf. also sect. 1.3). The lanthanide contraction was found to result for 86% from a nonrelativistic shell-structure effect and only for 14% from relativity. Results of similar calculations are available for YbH₂ (Pyykkö 1979a).

Lohr and Jia (1986) performed nonrelativistic SCF calculations on LaH₃ using basis sets between minimal and valence double-zeta quality. The molecule was found to have a C_{3v} equilibrium structure with a H–La–H bond angle of 115°, however the inversion barrier for a D_{3h} transition state was calculated to be only 239 cm⁻¹.

DiBella et al. (1993) also investigated LaH₃ with SCF, CASSCF and CISD calculations using a relativistic effective core potential from Hay and Wadt (1985b) for La. They obtained a C_{3v} equilibrium structure with a H–La–H bond angle of 113°. In good agreement with the all-electron work of Lohr and Jia (1986) the optimized planar D_{3h} structure was found to be 0.97 kcal/mol (339 cm⁻¹) higher in energy.

3.3.2. Oxides

DeKock et al. (1990) investigated the equilibrium structure of CeO₂ besides other AB₂ molecules using the quasirelativistic HFS method of the Amsterdam group (Ziegler et al. 1989). The bent structure (calc. $R_e = 1.82$ Å, $\phi_e \leq 132^\circ$; exp. $\phi_e = 146\pm2^\circ$, Gabelnick et al. 1974) is explained by the predominance of sd over sp and sf hybridization in agreement with earlier AB₂ molecular models of Walsh (1953) and Hayes (1966) for s and p as well as s, p and d orbitals, respectively. The explanation of the bent structure via a d-orbital participation is also in line with the conclusions reached by Wadt (1981) and Pyykkö et al. (1989) in their theoretical studies of the heavier homologue ThO₂. Although the 4f-orbital population in CeO₂ was found to be 1.3, the core-like nature of the 4f shell prevents an active role in bonding and a possible linear molecule. The electric multipole expansion method was shown to be unable to obtain the correct bent structure for CeO₂.

The gas-phase reactivity with respect to activation of saturated and unsaturated hydrocarbon substrates, thermochemistry and electronic structure of CeO_2^+ has been studied experimentally using Fourier-transform ion cyclotron mass spectrometry as well as theoretically using quasirelativistic density-functional and ab initio pseudopotential calculations (Heinemann et al. 1996). In contrast to CeO_2 , which is found to be bent (O–Ce–O bond angle 132°) and linear in relativistic and nonrelativistic calculations, respectively, the cation CeO_2^+ is calculated to be linear at all levels of theory. The calculated vertical ionization potentials, i.e. 9.02 eV from density-functional and 9.24 eV from pseudopotential configuration interaction calculations, are in excellent agreement with the experimental value of 9.40 ± 0.15 eV. Relativity is found both to lengthen and to strengthen the Ce–O bonds.

3.3.3. Halides

Numerous theoretical studies exist for the trihalides of the lanthanides. A few studies also treat the di- or tetrahalides. Self-consistent-charge extended Hückel calculations for all lanthanide trihalides RX₃ (R=La-Lu, X=F, Cl, Br, I) have been carried out by Myers et al. (1978). The f shell was assumed to be core-like and not explicitly included in the calculations. In qualitative agreement with most of the experimental evidence all molecules were found to be pyramidal with X-R-X angles of $91-92^{\circ}$ (X=F), 101-105° (Cl), 99–104° (Br) and 114–119° (I). The pyramidal geometries are mainly due to a better interaction between the R $5d_{r^2}$ and the X p orbitals with a concomitant enhanced covalency evidenced by a reduced positive charge on the metal when going from D_{3h} to C_{3v} symmetry. Bender and Davidson (1980) applied the semiempirical Wolfsberg-Helmholz molecular orbital method (Wolfsberg and Helmholz 1952) (energetic reference data from experiment, atomic orbitals from nonrelativistic calculations) to study orbital energies, charge distribution and $f \rightarrow d$ transition energies of the lanthanide trihalides RX₃ (R=Ce-Lu, X=F, Cl, Br, I). A planar D_{3h} equilibrium structure and fixed bond lengths estimated from atomic radii were assumed. Pyykkö and Lohr (1981) however found in agreement with experimental data a pyramidal C_{3y} structure for the triiodides RI₃ (R=La, Gd, Lu) using his quasirelativistic extended Hückel method. For fixed bond lengths the I-R-I bond angles increase from 100° to 106° for La to Lu. Li et al. (1983) used an INDO approach to investigate the electronic structure of the trifluorides RF_3 (R=Ce, Nd, Sm, Gd, Tb, Tm, Yb) assuming an idealized planar D_{3h} structure and fixed bond lengths taken from experiment. The authors discuss orbital energies and the results of a Mulliken population analysis. Covalent bonding between R and F was found to be due mainly to the R 5d and F 2p orbitals, to a lesser extent to the R 6s and 6p orbitals. The authors state that the R 4f orbitals almost do not participate in chemical bonding. The photoelectron spectra of some gaseous lanthanide trihalides [LaCl₃, RBr₃ (R = La, Ce, Nd, Lu), RI₃ (R = La, Ce, Nd, Er, Lu)] have been measured and assigned with the help of relativistic discrete variational Dirac-Hartree-Fock-Slater calculations by Ruščić et al. (1983). Ellis and Goodman (1984) also used the discrete-variational Dirac-Hartree-Fock-Slater method to calculate one-electron energies as well as charge and magnetization densities of $LaCl_3$ and other selected molecules RX_3 (R = La, Ce, Lu, X = Br, I) at their experimental geometries. The theoretical one-particle energies compare well with gas-phase photoelectron spectra. Lohr and Jia (1986) report results of quasirelativistic extended Hückel calculations for selected lanthanide trihalides RX₃ (R = La, Nd, Gd, Lu, X = F, Cl, Br, I) with fixed geometries taken from experiment. The authors compare orbital energies to experimental ionization potentials. They also present results of nonrelativistic all-electron SCF calculations for LaX_3 (X = F, Cl) using essentially minimal basis sets. LaF₃ was found to be pyramidal with a bond angle of 112° and a low inversion barrier of 921 cm⁻¹, whereas LaCl₃ was calculated to be planar.

Culberson et al. (1987) used their INDO/1 method to investigate equilibrium structures and ionization potentials of selected lanthanide halides RX_n (n=2,3,4). The overall accuracy for bond lengths is usually better than 0.05 Å, the values calculated for the

Molecule	R _e (Å)	$\phi_{ m e}$ (9	IP (eV)		
	INDO/1 ^b	exp. °	INDO/1 ^b	exp.°	INDO/1 ^b	exp. ^c	
EuCl ₂	2.576		143.3	130±15	5.3		
YbCl ₂	2.400		120.2	126±5	3.2		
CeF,	2.204	2.180	106.8		8.4	8.0	
CeCl ₃	2.570	2.569	115.6	111.6	10.0	9.8	
CeBr ₃	2.668	2.722	115.8	115.0	9.6	9.5	
CeI ₃	2.844	2.927	119.8		9.9		
GdCl ₃	2.154	2.489	110.0	113.0	17.7	15.5-16.5	
LuF3	2.045	2.020	107.4			19.0	
LuCI ₃	2.415	2.417	108.2	111.5	18.6	(17.4–18.7) ^d	
LuBr ₃	2.528	2.561	108.6	114.0	17.8	(16.8–18.4) ^d	
LuI ₃	2.726	2.771	115.6	114.5	17.7	(16.2–18.1) ^d	
CeF ₄	2.099	2.040	109.5	109.5			

 Table 35

 Comparison of bond lengths R_e , bond angles ϕ_e and ionization potentials IP for selected lanthanide halides calculated with INDO/1 method in comparison with available experimental data^a

^a Data from Culberson et al. (1987).

^b INDO/1, intermediate neglect of differential overlap calculations.

^c Experimental values from DeKock et al. (1972), Krasnov et al. (1978), Popenko et al. (1978), Ruščić et al. (1983), Beattie et al. (1983).

^d Estimated values, from Krasnov et al. (1976).

fluorides being too large, those for the iodines too small. Bond angles agree usually with the experimental values within 5° for the trihalides, whereas the larger deviations for the dihalides are still within the experimental error bars. The function of the energy depending on the out-of-plane angle is very flat and Culberson et al. estimate their bond angles converged to $\pm 3^{\circ}$. The experimental ionization potentials are reproduced with errors of a few tenths of an electron volt. It should be noted that the geometries of CeCl₃ and LuCl₃ were used for the parametrisation of the method and the excellent results for the trichlorides should be no surprise. The good performance of the method for the other molecules studied by Culberson et al. indicates a satisfactory transferability of the derived parameter sets. The authors emphasize that the inclusion of f orbitals is essential to obtain the bent and pyramidal structures of the di- and trihalides, respectively. In addition, the agreement for bond lengths is considerably improved when f orbitals are allowed to participate in chemical bonding. Part of the results of this study are listed in table 35.

PPs modeling di- and trivalent lanthanide atoms in molecules have been used by Dolg et al. (1989c,1991b) in PP SCF/CISD calculations to determine the equilibrium geometries and atomization energies of all lanthanide trifluorides and other di- and trihalides (RX₂, R=Eu, Yb, X=F, Cl, Br, I; RX₃, R=La, Eu, Gd, Yb, Lu, X=Cl, Br, I). A selection of the results is listed in table 36. LaF₃ was found to be pyramidal (C_{3v}) with a F–La–F bond angle of 116.6°. Since the inversion barrier was lower than 0.01 eV all other

			. 1				
Molecule	<i>n</i> (4f) ^b	R _e	(Å)	φ,	e (°) ^d	ΔE_{at}	(eV)
		calc.	exp.°	calc.	exp. ^c	calc.	exp. c
LaF ₃	0	2.159	2.22	116.6		18.17	19.81
LaCl ₃	0	2.612	2.62	(120)	111.6	13.80	15.88
LaBr ₃	0	2.770	2.74	(120)	115.0	11.86	13.71
LaI ₃	0	3.016	2.99	(120)		9.55	11.28
EuF ₂	7	2.170		129	110±15	10.31	11.40
EuCl ₂	7	2.654		141	130±15	7.53	9.11
EuBr ₂	7	2.839		153		6.22	
EuI ₂	7	3.083		161		6.49	6.76
GdF ₃	7	2.056	2.10	(120)		18.16	18.81
GdCl ₃	7	2.511	2.49	(120)	111.6	13.24	15.14
GdBr ₃	7	2.667	2.64	(120)	115.0	12.28	13.06
GdI₃	7	2.903	2.84	(120)		8.96	10.33
YbF ₂	14	2.100		138	140±15	9.85	
YbCl ₂	14	2.586		159	140±15	6.94	
YbBr ₂	14	2.759		180		5.61	7.81
YbI ₂	14	2.989		180		4.08	
LuF ₃	14	1.965	2.02	(120)		18.21	18.44
LuCl ₃	14	2.428	2.42	(120)	111.5	13.15	15.10
LuBr ₃	14	2.584	2.56	(120)	114.0	11.15	12.80
LuI ₃	14	2.819	2.77	(120)	114.5	8.78	10.67

Table 36

Bond lengths R_e , bond angles ϕ_e and atomization energies ΔE_{at} for selected lanthanide halides from pseudopotential configuration interaction calculations including the Langhoff-Davidson size-consistency correction in comparison with experimental data^a

^a Data taken from Dolg et al. (1989c, 1991b).

^b n(4f) is the fixed 4f occupation number modeled by the lanthanide pseudopotential

^c Experimental values from Hastie et al. (1971), DeKock et al. (1972), Hariharan and Eick (1972a,b), Hariharan et al. (1972), Petzel and Greis (1972), Myers (1975), Myers and Graves (1977).

^d Bond angles in parentheses have been kept fixed.

trihalides were assumed to be planar (D_{3h}) . The bond lengths of the trifluorides are too short by up to 0.06 Å, whereas those of the triiodides are too long by up to the same amount. For the other trihalides the agreement with experimental data is better. The trends in the experimental atomization energies are quite well reproduced, see, e.g., fig. 12 for the trifluorides. A higher percentage of the experimental values is recovered for the lighter halides than for the heavier ones: 90–100% for the trifluorides vs. 67–87% for the triiodides. In agreement with experimental evidence the difluorides and dichlorides of Eu and Yb are found to be bent (C_{2v}) . Whereas the agreement between the INDO/1 and the PP CISD results is reasonable for EuCl₂, larger deviations exist for YbCl₂. Experimental data for the bond length are not available, but two different values have been reported for the bond angle: 140±15° (DeKock et al. 1972) and >126±5° (Beattie



Fig. 12. Atomization energies for the lanthanide trifluorides from pseudopotential configuration interaction calculations (calc.) in comparison to experimental data (exp.). Data taken from Dolg et al. (1989c, 1991b).

et al. 1983). The first value is closer to the PP CISD result of 159°, whereas the latter agrees better with the INDO/1 result of 120°. For a more detailed discussion we refer to the original paper. The energy differences with respect to the linear geometry are rather small, i.e. 0.137 eV (EuF₂), 0.062 eV (YbF₂), 0.034 eV (EuCl₂) and 0.005 eV (YbCl₂). The dibromides and diiodides of Eu were predicted to be bent, whereas those of Yb should be linear. The energy gaps between the bent and linear equilibrium structures are even smaller: 0.015 eV (EuF₂) and 0.002 eV (EuI₂).

Among other triatomic molecules DeKock et al. (1990) investigated the equilibrium structure of YbCl₂ using the quasirelativistic Hartree–Fock–Slater approach developed by the Amsterdam group (Ziegler et al. 1989). The calculated bond length (2.40 Å) and bond angle (120°) agree perfectly with the INDO/1 results of Culberson et al. (1987) (2.40 Å, 120.2°). These results are in poor agreement with the PP CISD values of Dolg et al. (1991b). The optimized linear structure is higher in energy by 1.8 kcal/mol, which is by a factor of 16 larger than the PP CISD result. Upon bending the molecule the population of the Yb p and f orbitals decreases, whereas that of the s and d orbitals increases. From these results the authors conclude that sd hybridization favors bent structures, whereas sp and sf hybridization favor the linear geometry. These findings are in line with the models for AB₂ molecules advocated earlier by Hayes (1966) (s, p and d orbitals) or Walsh (1953) (s and p orbitals), they contradict however the statement by Culberson et al. (1987) that the bent geometry of YbCl₂ is due to a small amount of p-orbital hybridization. The derived atomization energy of 6.68 eV agrees well with the PP CISD result of 6.94 eV.

DiBella et al. (1993) performed SCF, CASSCF and CISD calculations for LaF₃ and LaCl₃. A relativistic effective-core potential of Hay and Wadt (1985b) was used for La, whereas F and Cl were treated at the all-electron level. LaF₃ was found to be slightly pyramidal (F–La–F bond angle 118.5°, inversion barrier 0.04 kcal/mol), whereas LaCl₃ was calculated to be planar. The increasing tendency towards a planar geometry in the

series LaH₃, LaF₃ and LaCl₃ was attributed to the different σ and π donor capabilities of the ligands. Interaction of ligand σ orbitals with the metal d_{xz}, d_{yz} orbitals is only possible for C_{3v} symmetry, whereas ligand π orbitals can interact best in D_{3h} geometry with orbitals on La. The increase of the π donor capabilities from F⁻ to Cl⁻ explains the calculated and experimentally observed equilibrium structures.

3.3.4. Sandwich complexes

The organometallic chemistry of f-block elements has attracted much attention from experimentalists and theoreticians during the last 25 years (Marks 1978, Marks and Fischer 1979, Marks and Ernst 1982). Di- π -cyclooctatetraeneuranium(IV) U(C₈H₈)₂ (uranocene) was the first actinocene to be synthesized (Streitwieser and Müller-Westerhoff 1968). The synthesis of Di- π -cyclooctatetraenethorium(IV) Th(C₈H₈)₂ (thorocene) was reported in the next year (Streitwieser and Yoshida 1969). Hodgson et al. (1973) published the preparation of lanthanide π -carbocyclic complexes of the formula K[Ln(C₈H₈)₂] (Ln=Y, La, Ce, Pr, Nd, Sm, Gd, Tb), thus extending the field of organometallic sandwich compounds to the lanthanides. The thorocene homologue Ce(C₈H₈)₂ (cerocene), presumably corresponding to di- π -cyclooctatetraenecerium(IV), was synthesized by Greco et al. (1976).

The actinocenes were shown to be isostructural having D_{8h} symmetry. It was this high symmetry as well as the speculation on d and f orbital participation in metal-ring bonding which caused the interest of several theoreticians. Uranocene was originally expected to be an f-element analogue of d-element metallocenes like di- π -cyclopentadieneiron(II) Fe(C₅H₅)₂ (ferrocene), where covalent ring-metal interactions result from the interaction of metal d orbitals with ligand π orbitals (Streitwieser and Müller-Westerhoff 1968). The anionic lanthanocenes synthesized by Hodgson et al. (1973) were found to be more ionic than the actinocenes, i.e. they exhibit a lower metal-ring covalency. It was a surprising result, therefore, that based on several theoretical criteria cerocene shows a substantial covalency and an f-orbital contribution to metal-ring bonding comparable to uranocene (Rösch 1984, Streitwieser et al. 1985).

The accurate treatment of transition metal sandwich compounds is a considerable challenge for ab initio quantum chemistry. For example, it took about a decade and numerous large-scale calculations using different electron correlation methods until recently the metal-ring distance of ferrocene was obtained by Park and Almloef (1991) in satisfactory agreement with the experimental value. Studies on the lanthanide and actinide sandwich compounds appear to be even more complicated. This is due to the larger effects of relativity and electron correlation.

Ortiz and Hoffmann (1985) used the extended Hückel method to study the cyclopentadiene complexes $\text{Sm}(\text{cp})_2^{q+}$ (q=0,1) and $(\text{SmH}(\text{cp})_2)_n$ (n=1,2) ($\text{cp}=\text{C}_5\text{H}_5$). $\text{Sm}(\text{cp})_2$ was found to have an ordinary sandwich structure with a ring-metal-ring angle of 180°; distortions of the ring-metal-ring angle are not energetically costly, however. According to Ortiz and Hoffmann in their applications the 4f orbitals have no chemical importance with respect to the molecular structures.

Kaupp et al. (1993) studied the equilibrium structures of group-2 and lanthanide (II) metallocenes $M(cp)_2$ (M=Ca, Sr, Ba, Sm, Eu, Yb) using quasirelativistic PPs for a fixed 4f occupation at the SCF, MP2 and CISD levels. Experiments showed that the solventfree permethylated metallocenes $M(cp^*)_2$ ($cp^* = C_5(CH_3)_5$) of these elements have ringmetal-ring bond angles of less than 180°, i.e. they do not exhibit the idealized 'linear' D_{5h} or D_{5d} equilibrium structures, however they maintain the η_5 coordination of the metal to the rings. At the SCF level all molecules have a 'linear' structure, whereas in MP2 calculations some of the molecules are found to have a 'bent' structure, e.g. ring-metalring angles of 164°, 175° and 180° were found for the Sm, Eu and Yb compounds, respectively. The corresponding experimental values from X-ray spectroscopy of the solids or gas-phase electron diffraction range from 140° to 160°. The structure of the Sm compound is in disagreement with the EHT results of Ortiz and Hoffmann (1985). However, the bending potential curves are extremely shallow and the energies required for linearization (if any) are of the order of a few kJ/mol. These flat potentials should allow large-amplitude bending motions and explain the 'bent' gas-phase thermal average structures of these floppy molecules.

Strittmatter and Bursten (1991) performed quasirelativistic X_{α} scattered-wave calculations using the scalar Wood–Boring Hamiltonian (Boring and Wood 1979a,b) on the actinide complexes A(cp)₃ (A=U, Np, Pu, Am, Cm, Bk, Cf) and compared the results to those for the related lanthanide compounds R(cp)₃ (R=Ce, Pr, Nd, Sm, Gd, Dy). C_{3v} symmetry was assumed. Due to their smaller radial extent the bonding ability of the 4f orbitals with the η^5 -bonded ligands is only 60–70% of the actinide 5f-orbital interaction, however it is roughly the same for the lanthanide 5d and actinide 6d orbitals. In contrast to the actinide 7s orbital the lanthanide 6s orbital is found to have no influence in bonding. The semi-core 5p orbitals of the lanthanides were found to have a greater antibonding influence on the ligands than the 6p orbitals of the actinides. The orbital energies of the 4f and 5d metal orbitals of the compounds with early lanthanides resemble those of the 5f and 6d metal orbitals of the complexes with middle actinides, whereas the molecules with late lanthanides are similar to those with late actinides. This is consistent with the lanthanide-like behavior of the late actinide elements (Cotton and Wilkinson 1988).

The results of INDO calculations for the bis(cyclooctatetraene)cerium(III) anion with an idealized D_{8h} geometry were published by Clack and Warren (1976). The calculations indicated that the 4f orbitals are essentially localized at the formally Ce³⁺ central ion, their overall ligand field splitting being less than 500 cm⁻¹. The 5d-orbital participation to the high-lying a_{1g} , e_{1g} and e_{2g} ligand orbitals of π character was calculated to be 3%, 27% and 29% indicating significant covalency. In earlier studies of this system Warren (1975) used the ligand field approach assuming $D_{\infty h}$ symmetry of the ligands.

A single lanthanide (IV) metallocene, i.e. bis(cyclooctatetraene)cerium(IV) Ce(C₈H₈)₂ or cerocene, has been studied theoretically. Rösch and Streitwieser (1978,1983) reported the results of nonrelativistic and quasirelativistic scattered-wave X_{α} calculations taking into account the scalar relativistic effects for cerocene, thorocene and uranocene at fixed idealized D_{8h} geometries (fig. 13). The authors discuss the participation of metal d and f



Fig. 13. Idealized D_{8h} structure of cerocene. (H, white; C, grey; Ce, grey, small).

orbitals to metal-ring bonding as well as the assignment of photoelectron and optical absorption spectra. Thereafter, the results of these calculations were discussed by Rösch (1984) and additional experimental data on cerocene have been reported by Streitwieser et al. (1985). In the following we will focus mainly on cerocene and the heavier homologue thorocene. For information on uranocene as well as other actinocenes we refer the reader to the reviews by Pepper and Bursten (1991) and Balasubramanian (1994). Examples for ab initio studies are those of Boerrigter et al. (1988), A.H.H. Chang and Pitzer (1989) or A.H.H. Chang et al. (1994).

Assuming a completely ionic model, i.e. M^{4+} complexed by two $C_8H_8^{2-}$ ligands, the highest and next-highest occupied ligand orbitals have π character and transform according to the e_{2u} and e_{2g} representations of the D_{8h} point group. The metals have lowlying empty s (a_{1g}) , p (a_{2u}, e_{1u}) , d (a_{1g}, e_{1g}, e_{2g}) and f $(a_{2u}, e_{1u}, e_{2u}, e_{3u})$ orbitals. Therefore, the most important covalent contributions to metal-ring bonding may arise from metal d (e_{2g}) and f (e_{2u}) orbitals interacting with the ligand π orbitals of the same symmetry. Since d and f orbitals are relativistically more destabilized for Th than for Ce, i.e. they are more diffuse and accessible for bonding, one expects larger covalent contributions for thorocene than for cerocene. Therefore, cerocene should be more ionic than thorocene. In his X_a studies Rösch (1984) indeed found an increase in relativistic effects according to Ce < Th, however he concluded that for a roughly constant d-orbital covalency the f-orbital covalency increases as Th < Ce, whereas the ionicity is in the order Ce < Th. These findings obviously initiated further experimental work (Streitwieser et al. 1985) on cerocene. The authors note that the existence of cerocene should be regarded as being remarkable: the compound combines a strong reducing agent (two C₈H₈²⁻ rings) with a powerful oxidizing agent (Ce⁴⁺). Based on the product pattern of the hydrolysis, the

electronic absorption spectrum and the He I and He II photoelectron spectra Streitwieser et al. conclude that cerocene does not have the structure of a simple ionic cluster but shows substantial metal-ring covalency. This is in contrast to organolanthanide (II) or (III) compounds which are essentially ionic systems.

Dolg et al. (1991d, 1995) reported results of large-scale state-averaged PP MCSCF, MRCI, ACPF and DGCI calculations for the ground states and low-lying excited states of the bis(cyclooctatetraene)f-element sandwich complexes cerocene $Ce(C_8H_8)_2$ and thorocene $Th(C_8H_8)_2$. The initial motivation for these ab initio calculations was the original paper by Neumann and Fulde (1989) who claimed that for a single-determinant wavefunction cerocene rather corresponds to a compound of a formally trivalent cerium, i.e. a Ce³⁺ central ion which is complexed by two $C_8H_8^{1.5-}$ rings. The Ce³⁺ ion has an unpaired electron in an atomic-like 4f orbital, whereas the hole in the π HOMO of the ligands is delocalized over both eight-membered rings. When cerocene is described by a multi-determinant configuration interaction wavefunction, admixture of the $Ce^{4+}(C_8H_8^{2-})_2$ configuration to the leading $Ce^{3+}(C_8H_8^{1.5-})_2$ configuration lets the ${}^1A_{1g}$ fall below the lowest triplet state, i.e. ³E_{2g}. The resulting ¹A_{1g} ground state corresponds to a Ce^{III} compound which would be a molecular analogue of a Kondo singlet state known from solid-state physics. According to Neumann and Fulde the small singlet-triplet separation would cause the magnetic susceptibility to show a Van-Vleck type paramagnetism up to temperatures of approximately 10K. It should increase for temperatures above 10K and transform into a typical Curie susceptibility above 30K. The specific heat should show a typical Schottky anomaly. In addition cerocene has a lower ionicity as well as a higher f-orbital contribution to metal-ring bonding than one would expect for a Ce^{IV} compound. In contrast to cerocene the heavier homologue thorocene may be pictured as a Th^{IV} compound, i.e. a Th⁴⁺ closed-shell ion complexed by two aromatic $C_8H_8^{2-}$ ligands.

The model for cerocene suggested by Neumann and Fulde (1989) is supported by large-scale PP SCF calculations with up to 574 basis functions. The PPs modeled fixed 4f occupation numbers of 0 and 1 at cerium and the corresponding geometries were optimized (Dolg et al. 1991d). When estimates for electron correlation effects derived from correlation energy functional calculations or limited CEPA-1 calculations are added, the $4f^0\pi^4$ SC is found to be 0.84–1.84 eV and 1.86 eV higher in energy than the $4f^1\pi^3$ SC, respectively. In MCSCF calculations treating the 4f shell explicitly the lowest state was found to be a $4f_{a2u}^1\pi_{e2u}^3 E_{2g}$ state when only the $4f^1\pi^3$ SC was considered. The highest state of this superconfiguration was the ¹A_{1g} state with a term energy of 0.58 eV. Allowing the admixture of the $4f^0\pi^4$ SC brings this state at a term energy of $-0.56\,\text{eV}$ with respect to ${}^{3}E_{2g}$ (table 37). The mixing coefficients of the two SCs are 82.8% $4f_{e^{2}u}^{1}\pi_{e^{2}u}^{3}$ and 17.2% $4f^0\pi_{e_{2u}}^4$. Spin-orbit interaction was calculated to reduce the singlet-triplet splitting by $0.09 \,\text{eV}$, yielding a best estimate of $0.47 \,\text{eV}$ for the separation between the A_{1g} ground state and the E_{1g} and E_{2g} excited states. It is seen from table 38 that the ground state is by more than 99% a singlet, whereas the first excited state has 79% triplet and 21% singlet contributions. The results are in qualitative agreement with those of Neumann and Fulde (1989), however the quantitative agreement is poor. Neumann and Fulde estimated a 10 eV energy difference between the $4f^{1}\pi^{3}$ and $4f^{0}\pi^{4}$ SCs and obtained only

State		$T_{\rm e}$ (eV)			$\omega_{\rm c}$ (cm ⁻¹)
	MRCIS ^{b,c}	MCSCF ^{b,d}	MCSCF ^b		-e ()
¹ A _{1g}	-1.384	0.561	-0.658	2.088	186
³ E _{2g}	0.000	0.000	0.000	2.138	195
${}^{1}E_{2g}$	0.028	0.031	0.020	2.139	196
³ E _{1g}	0.060	0.061	0.063	2.139	196
³ E _{3g}	0.064	0.062	0.064	2.139	194
${}^{1}E_{1g}$	0.064	0.088	0.077	2.139	194
¹ E _{3g}	0.066	0.081	0.070	2.139	194
³ E _{1g}	0.131	0.092	0.080	2.143	193
¹ E _{1g}	0.137	0.121	0.088	2.143	194
³ E _{3g}	0.145	0.093	0.081	2.143	193
¹ E _{3g}	0.167	0.142	0.114	2.144	194
$^{3}A_{1g}$	0.348	0.210	0.225	2.150	196
${}^{3}B_{2g}$	0.357	0.219	0.234	2.150	196
${}^{3}B_{1g}$	0.382	0.226	0.243	2.150	196
${}^{3}A_{2g}$	0.384	0.235	0.252	2.151	195
${}^{1}A_{2g}$	0.384	0.251	0.252	2.151	196
${}^{1}B_{1g}$	0.385	0.254	0.255	2.151	196
${}^{1}B_{2g}$	0.398	0.258	0.260	2.151	196
$^{1}A_{1g}$	(3.737)	(6.630)			

Table 37

Results of MRCIS and MCSCF calculations for term energies T_e of electronic states resulting from the $4f^1\pi_{e2u}^3$ and $4f^0\pi_{e2u}^4$ superconfigurations of cerocene, and optimized cerium-ring distances d_e and vibrational frequencies ω_e for the A_{1e} cerium-ring stretching mode^a

^a Reproduced from Dolg et al. (1991d, 1995).

^b MRCIS, single excitation multi-reference configuration interaction;

MCSCF, multi-configuration self-consistent field calculations; all calculations are without spin-orbit coupling

^c Cerium-ring distance 2.08 Å.

^d Cerium-ring distance 2.20 Å.

a 6 meV singlet-triplet splitting between ground and first excited state which is two orders of magnitude smaller than that found in the ab initio calculations. In agreement with the ab initio results a Kondo-type behavior of cerocene is not observed experimentally.

Large-scale PP MRCI and MRACPF calculations with 202 basis functions and up to 52 correlated electrons in 173 molecular orbitals yielded, after correction for spin-orbit effects, a singlet-triplet splitting of 1.00 eV (Dolg et al. 1995), which is approximately twice as large as the previous MCSCF result. The authors also discuss the interpretation of experimental optical absorption as well as photoelectron spectra, which are both consistent with the assumption that cerocene is actually better described as di- π -cyclooctatetraenecerium(III).

Smaller singlet-triplet splittings and a possible Kondo analogue behavior of a molecule should be found for systems where the ligand orbitals are more extended and couple

Table 38

Term energies of electronic states resulting from the $4f^1\pi_{e2u}^3$ and $4f^0\pi_{e2u}^4$ superconfigurations of cerocene from configuration interaction calculations with spin-orbit coupling, and contributions of single-group adapted states to double-group adapted states^a

State	$T_{\rm e}$ (eV)	Contributions of AS states ^b
A _{1g}	-1.294	99 ⁱ A _{1g}
E_{1g}	0.0	57 ${}^{3}E_{2g}$, 22 ${}^{3}E_{1g}$, 20 ${}^{1}E_{1g}$, 1 ${}^{1}E_{1g}$
E_{2g}	0.0	57 ³ E _{2g} , 21 ³ E _{1g} , 22 ³ E _{3g}
E _{3g}	0.003	57 ${}^{3}E_{2g}$, 22 ${}^{3}E_{1g}$, 21 ${}^{1}E_{3g}$
E_{2g}	0.015	50 ${}^{1}E_{2g}$, 26 ${}^{3}E_{1g}$, 24 ${}^{3}E_{3g}$
E _{lg}	0.118	$1 {}^{3}E_{2g}$, $8 {}^{3}E_{1g}$, 23 ${}^{1}E_{1g}$, 40 ${}^{3}E_{1g}$, 23 ${}^{1}E_{1g}$, 6 ${}^{3}A_{1g}$
A _{2g}	0.118	$3 {}^{3}E_{1g}, 94 {}^{3}E_{1g}, 3 {}^{3}A_{1g}, 1 {}^{1}A_{2g}$
A _{1g}	0.124	$2 {}^{3}E_{1g}, 94 {}^{3}E_{1g}, 4 {}^{3}A_{2g}$
E _{3g}	0.127	$1 {}^{3}E_{3g}$, $1 {}^{1}E_{3g}$, 49 ${}^{1}E_{3g}$, 46 ${}^{3}E_{3g}$, 3 ${}^{3}B_{2g}$, 1 ${}^{3}B_{1g}$
B_{1g}	0.129	$3 {}^{3}E_{3g}, 93 {}^{3}E_{3g}, 3 {}^{3}B_{2g}, 1 {}^{1}B_{1g}$
B_{2g}	0.130	$1 {}^{3}\mathbf{E}_{3g}, 95 {}^{3}\mathbf{E}_{3g}, 1 {}^{3}\mathbf{B}_{1g}, 2 {}^{1}\mathbf{B}_{2g}$
A_{2g}	0.146	83 ${}^{3}E_{1g}$, 3 ${}^{3}E_{1g}$, 7 ${}^{3}A_{1g}$, 8 ${}^{1}A_{2g}$
E _{3g}	0.151	42 ${}^{3}E_{3g}$, 42 ${}^{1}E_{3g}$, 1 ${}^{1}E_{3g}$, 1 ${}^{3}E_{3g}$, 7 ${}^{3}B_{2g}$, 8 ${}^{3}B_{1g}$
B _{1g}	0.154	83 ${}^{3}E_{3g}$, 3 ${}^{3}E_{3g}$, 6 ${}^{3}B_{2g}$, 8 ${}^{1}B_{1g}$
B_{2g}	0.156	86 ${}^{3}E_{3g}$, 1 ${}^{3}E_{3g}$, 7 ${}^{3}B_{1g}$, 6 ${}^{1}B_{1g}$
E_{1g}	0.162	$2 \ {}^{3}E_{2g}$, $39 \ {}^{3}E_{1g}$, $18 \ {}^{1}E_{1g}$, $13 \ {}^{3}E_{1g}$, $15 \ {}^{1}E_{1g}$, $4 \ {}^{3}A_{1g}$, $9 \ {}^{3}A_{2g}$
A _{1g}	0.177	93 ${}^{3}E_{1g}$, 3 ${}^{3}E_{1g}$, 3 ${}^{3}A_{2g}$
E_{2g}	0.224	43 ${}^{3}E_{2g}$, 28 ${}^{3}E_{1g}$, 29 ${}^{3}E_{3g}$
Elg	0.226	41 ${}^{3}E_{2g}$, 23 ${}^{3}E_{1g}$, 30 ${}^{1}E_{1g}$, 3 ${}^{3}E_{1g}$, 3 ${}^{1}E_{1g}$
E_{3g}	0.227	43 ${}^{3}E_{2g}$, 28 ${}^{3}E_{3g}$, 29 ${}^{1}E_{3g}$
E _{2g}	0.237	50 ${}^{1}E_{2g}$, 25 ${}^{3}E_{1g}$, 25 ${}^{3}E_{3g}$
E_{2g}	0.323	100 ³ E _{1g}
E_{3g}	0.333	48 ${}^{1}E_{3g}$, 52 ${}^{3}E_{3g}$
E _{2g}	0.338	100 ³ E _{3g}
E _{lg}	0.341	$2 {}^{1}E_{1g}$, $43 {}^{3}E_{1g}$, $54 {}^{1}E_{1g}$, $1 {}^{3}A_{2g}$
A _{2g}	0.436	$14 {}^{3}E_{1g}$, 56 ${}^{3}A_{1g}$, 29 ${}^{1}A_{2g}$
\mathbf{E}_{1g}	0.440	$7 \ {}^{3}E_{1g}, \ 7 \ {}^{1}E_{1g}, \ 2 \ {}^{1}E_{1g}, \ 57 \ {}^{3}A_{1g}, \ 27 \ {}^{3}A_{2g}$
E _{3g}	0.441	$7 \ {}^{3}E_{3g}, \ 7 \ {}^{1}E_{3g}, \ 52 \ {}^{3}B_{2g}, \ 34 \ {}^{3}B_{1g}$
\mathbf{B}_{1g}	0.445	$14 \ {}^{3}E_{3g}$, $54 \ {}^{3}B_{2g}$, $32 \ {}^{1}B_{1g}$
B_{2g}	0.462	13 ${}^{3}E_{3g}$, 50 ${}^{3}E_{3g}$, 37 ${}^{1}B_{1g}$
A _{1g}	0.507	$4 {}^{3}E_{1g}$, $2 {}^{3}E_{1g}$, 93 ${}^{3}A_{2g}$
\mathbf{E}_{1g}	0.546	$2 \ {}^{3}E_{1g}, \ 3 \ {}^{1}E_{1g}, \ 33 \ {}^{3}A_{1g}, \ 63 \ {}^{3}A_{2g}$
A_{2g}	0.548	$4 {}^{3}E_{1g}$, $34 {}^{3}A_{1g}$, $62 {}^{1}A_{2g}$
E _{3g}	0.550	$2 {}^{1}E_{3g}, 2 {}^{3}E_{3g}, 38 {}^{3}B_{2g}, 58 {}^{3}B_{1g}$
\mathbf{B}_{1g}	0.555	$4 {}^{3}E_{3g}, 37 {}^{3}B_{2g}, 59 {}^{1}B_{1g}$
\mathbf{B}_{2g}	0.566	$3 {}^{3}E_{3g}$, 42 ${}^{1}B_{1g}$, 55 ${}^{1}B_{2g}$

^a Reproduced from Dolg et al. (1995).
 ^b Contributions are given when ≥1%, in order of energy according to table 37.



Fig. 14. Idealized D_4 structure of cerium-di-phthalocyanine (H, white; C, grey; N, black; Ce, grey, small). The ring-ring distance has been artificially increased for clarity.

weaker to the f orbitals on cerium. It is supposed that such a system is di- π phthalocyaninecerium(III). Preliminary PP SCF calculations (Dolg 1995) including the 4f shell in the core indicate that the ground-state SC indeed corresponds to a Ce³⁺ central ion with a 4f¹ occupation and a singly occupied ligand orbital. The closed-shell configuration with a Ce⁴⁺ ion is approximately 3 eV higher in energy. The staggered arrangement (D_{4h}) of the rings was found to be more stable by approximately 1 eV than the eclipsed conformation D_{4d} when the changes in the metal-ring distance were accounted for. However, in neither of these two symmetries is mixing of the highest occupied ligand orbital with a metal f orbital allowed due to symmetry reasons, i.e. a Kondo singlet state cannot be formed. Experimentally it is found that the rings are twisted by 38° (Haghighi et al. 1992). In a corresponding idealized D₄ symmetry (fig. 14) the required mixing would be possible and a singlet ground state could be formed. Attempts are currently being made to investigate this by means of limited CI calculations, which is not a trivial task for a system of 113 atoms having a relatively low symmetry. There is also some experimental evidence that configuration interaction is important for this system (Isago and Shimoda 1992).

The dimer of $bis(\eta^5$ -methylcyclopentadienyl)ytterbium chloride has been investigated with the INDO method (Li et al. 1987a). The weak interaction between the Yb atoms is due to chlorine bridges and not to a Yb-Yb bond.

Recently a modified quasirelativistic extended Hückel method was applied to investigate the structure of $bis(\eta^5$ -pentamethylcyclopentadienyl)samarium (Boudreaux and Baxter 1994). The authors were led to the conclusion that van der Waals forces play the dominant role for the ring–Sm–ring bond angle.

3.3.5. Fullerene complexes

Since the discovery of C_{60} (Kroto et al. 1985) empty fullerenes and fullerenes with encapsulated metal atoms have attracted much attention of theoreticians and experimentalists. We cannot even cite all important articles in this quickly expanding field and we merely concentrate on the few quantum-chemical studies of endohedral lanthanide–fullerene complexes.



Fig. 15. Structure of $M \otimes C_{28}$. Atoms forming a tetrahedron are shown black. Coordinates taken from Rösch et al. (1993).

 C_{28} appears to be the smallest experimentally important fullerene (Zhang et al. 1986) and forms endohedral complexes $M@C_{28}$ of increasing stability with the tetravalent metals Ti, Zr and Hf as well as with U (Chai et al. 1991). (The symbol @ in $M_{@}C_{n}$ is commonly used to indicate that the atom M is inside the C_n cage.) A tetrahedral symmetry has been proposed for the C₂₈ cage (Guo et al. 1992). The trend in the relative stabilities might be explained by an increasing overlap between metal orbitals and cage orbitals for an increasing size of the endohedral atom. The metal-cage bonding could be achieved by bonds between the endohedral metal and either four cage carbons forming an tetrahedron (fig. 15) (sp³, sd³ or sf³ hybridization at M) or six pairs of cage carbons with bond midpoints forming an octahedron (fig. 16) (sp³d² or sd²f³ hybridization at M) (Rösch et al. 1993). Symmetry considerations are helpful to estimate contributions to metal-ligand bonding in highly symmetric systems like complexes of arenes $(M(C_nH_n)_2, n=5, 8)$ or fullerenes $(M@C_n, n=28, 60, 82)$. In case of a tetrahedral C₂₈ cage the 8a1 and 14t₂ orbitals are singly occupied and coupled to give a quintet state. The metal s and f orbitals can mix with these two cage orbitals, respectively. Rösch et al. (1993) quantitatively investigated the bonding for the example $Ce_{@}C_{28}$ using the scalar quasirelativistic extension (Knappe and Rösch 1990, Rösch and Häberlen 1992, Häberlen and Rösch 1992) of the linear combination of Gaussian-type orbitals local densityfunctional (LCGTO-LDF) method (Dunlap and Rösch 1990). According to a Mulliken population analysis the three energetically highest occupied orbitals (13a₁, 20t₂ and 7t₁) of the closed-shell ground state showed metal f-orbital contributions of roughly 10%. Lowerlying orbitals of t₂ and e symmetry also show considerable metal d-orbital contributions of up to 18%. The mixing of metal s and p orbitals with cage orbitals is less important. Rösch et al. conclude that the Ce atom forms strong bonds to both groups of cage carbons with tetrahedral and octahedral symmetry. In contrast to the small Ti atom which is at an



Fig. 16. Structure of $M_{@}C_{28}$. Pairs of atoms with the bond midpoints forming an octahedron are shown black. Coordinates taken from Rösch et al. (1993).

off-center position bound to one of the tetrahedral cage-carbon atoms, Ce is large enough to stay in the center and form equally strong bonds to all four tetrahedral cage-carbon atoms. The authors also give some predictions concerning the photoelectron spectrum of Ce@C₂₈. Ab initio PP SCF/DGCI calculations including spin-orbit coupling on the corresponding actinide complex U@C₂₈ have recently been reported by A.H.H. Chang et al. (1994).

Rosén and Wästberg (1988, 1989) carried out density-functional calculations, using the discrete variational method and the self-consistent charge approximation, for $La@C_{60}^{q}$ (q=-1,0,+1) (fig. 17). The calculated ionization potentials and electron affinities are in rather good agreement with available experimental data. In the neutral system the lanthanum atom carries a charge of +2.85, i.e. formally all three valence electrons are transferred to the cage. To the authors' understanding relativistic effects have not been accounted for in this study.

The restricted Hartree–Fock (RHF) effective-core potential calculations by A.H.H. Chang et al. (1991) on low-lying electronic states of $M@C_{60}$ and $M@C_{60}^+$ (M=O, F, K, Ca, Mn, Cs, Ba, La, Eu, U) have already been reviewed by Balasubramanian (1994) in this Handbook. The calculations were carried out for an idealized icosahedral symmetry (I_h) with basis sets of in most cases valence double zeta quality. Spin–orbit coupling as well as electron correlation effects had to be neglected due to the size of the systems under study. La is found to lose two electrons from the 6s orbital to the cage lowest unoccupied orbital which has t_{1u} symmetry and to keep one electron in a 5d (h_g) orbital. Alternatively La might only lose one 6s electron to the t_{1u} cage orbital and promote the other into the La 5d (h_g) orbital. For both possibilities only a configurational average over several quartet states could be calculated and, since almost identical energies were found, no assignment for the ground state configuration was possible. Nevertheless, both possibilities are in



Fig. 17. Structure of M@C₆₀.

disagreement with the earlier work by Rosén and Wästberg (1988, 1989), who found a t_{1u}^3 ground-state configuration. This was attributed by Chang et al. to a failure of local density-functional theory to give reliable term energies for cases where closely spaced orbitals have different occupations. Configurations with an occupied 4f or 6s orbital on La were calculated to have considerably higher energies. Chang et al. found that Eu loses two electrons essentially from the 6s orbital to the t_{1u} lowest unoccupied cage orbital. The Eu^{2+} ion keeps a $4f^7$ $(t_{2u}^3g_u^4)\ ^8S$ substate and together with the $C_{60}^{2-}\ t_{1u}^2\ ^3T_{1g}$ substate forms a $^{10}T_{1u}$ ground state. The $^{10}T_{1g}$ first excited state corresponds to the situation when only one electron is transferred from Eu to the C_{60} cage and is 0.62 eV higher in energy. All compounds considered by Chang et al. were calculated to be unbound with respect to C₆₀ and M. The La compound is 1.8 eV and 3.0 eV more stable than the Eu and U complex, respectively. The ground-state configuration of the U complex results from a transfer of one U 7s electron to the t_{1u} lowest unoccupied cage orbital and the other 7s electron to the 6d (h_g) orbital. Since relativistic effects increase from La over Eu to U and significantly stabilize the metal s orbitals, which are occupied in the neutral atom but not in the complex, we assume that this order of relative stabilities is actually a relativistic effect. The trend is further enhanced by the relativistic destabilization of the metal d orbitals, whereas the cage orbitals remain unaffected.

A.H.H. Chang et al. (1991) also considered the cations $M@C_{60}^+$. With the exception of the Mn compound, ionization occurs from cage t_{1u} orbitals, occupied with one or two electrons in the neutral species. The authors predict that the range of the chemically accessible M oxidation states is limited by the presence of the cage, i.e. formally La (II) instead of La (III) compounds are to be expected. With dissociation energies of -1.70 eV and -2.27 eV, and ionization potentials of 4.81 eV and 4.74 eV, the Ba and Eu compounds are rather similar.

It has been experimentally observed that lanthanum-containing (endohedral) fullerenes La@C_n have a unique stability for n=82, despite the fact that the cages with the magic numbers n = 60, 70 and 84 appear to be more stable and more abundant than that with n=82 (Chai et al. 1991). La@C₈₂ was found to be the only lanthanum-fullerene which is stable with respect to moisture and air. It was suggested that La formally donates two electrons to the cage to form a closed-shell C_{82}^{2-} cage isoelectronic with the stable C_{84} fullerene. A 5d¹ configuration was assumed for the encapsulated La²⁺ ion. On the other hand the hyperfine structure observed in electron paramagnetic resonance (EPR) measurements (Johnson et al. 1992) suggest a La³⁺ ion and a C_{82}^{3-} cage. Nagase et al. (1993) therefore investigated the relative stabilities of C₈₂ isomers and the electronic structure of LaC₈₂ using the semiempirical Austin Model 1 (AM1) method (Dewar et al. 1985) and ab initio unrestricted Hartree-Fock (UHF) self-consistent field calculations, respectively. The authors used the AM1 method to establish the relative stability of seven of the nine possible isomers of C_{82} which have no adjacent pentagons. They found a C_2 structure to be the most stable and used the optimized geometry in their subsequent studies on the RC₈₂ systems (Nagase et al. 1993, Nagase and Kobayashi 1993, 1994). We note, however, that two other structures with C_2 symmetry as well as two structures with C_s symmetry were found at energies higher by 12 kcal/mol or less. The authors performed ab initio calculations using basis sets of double-zeta quality and the quasirelativistic large-core effective core potential of Hay and Wadt (1985a) for lanthanum. The most stable position of the lanthanum atom was found to be about 1.75 Å off the center of the cage, only 2.36-2.44 Å away from six carbons of the cage forming a hexagon. This off-center position was found to be more stable by about 54 kcal/mol than the center position. At this energetically most favorable position the Mulliken charge on La is +2.7, supporting a formal $La^{3+}C_{82}^{3-}$ charge distribution. The authors found a local minimum about 1.35 Å from the center of the cage and about 40 kcal/mol more stable than the center position. In this position lanthanum keeps one 5d orbital singly occupied and the formal charge distribution corresponds to $La^{2+}C_{82}^{2-}$. The position of La outside the cage (exahedral structure) above a cage hexagon was found to be only slightly more stable than the center position of the encapsulated La (endohedral structure). The ionization potential was calculated to be 7.1 eV and 5.4 eV for C82 and $La@C_{82}$. This indicates that $La@C_{82}$ is a good electron donor and together with good electron acceptors like empty fullerenes might form complexes of the type La@C⁺₈₂C⁻_n in solution.

The complex La_@C₈₂ was also investigated by Laasonen et al. (1992) using the Car– Parrinello method (Car and Parrinello 1985) which is based on local density-functional theory. The scalar relativistic effects were considered for the lanthanum central metal by use of the norm-conserving PP of Bachelet et al. (1982). C_{3v} symmetry was assumed for the cage, although this isomer is not the most abundant. The authors found that in agreement with experimental data the central ion is essentially La³⁺ and the unpaired electron is delocalized on the cage. The lanthanum ion is in a low-symmetry off-center position and coordinated to cage-carbon atoms. The high-symmetry center position is about 3.5 eV higher in energy and the central ion is formally La^{2+} , the unpaired electron remaining in a metal 5d orbital.

In a related study Nagase and Kobayashi (1993) investigated the metallo-fullerenes RC_{82} with R = Sc, Y and La. The small-core effective-core potentials of Hay and Wadt (1985b) were applied for the metal atoms. The AM1 optimized C_2 geometry of the cage was kept fixed. The UHF calculations for La@C₈₂ led to a equilibrium geometry with La about 1.40 Å from the center of the cage. The Mulliken charge on the metal was +2.90, corresponding to a La³⁺C³⁻₈₂ charge distribution. Similar equilibrium structures with the metal in an off-center position and corresponding stabilization energies were found for Sc and Y, however the Mulliken charges on the metal were only +1.97 and +2.42. Based on these values and the nearly integral d-orbital populations of 1.07 for Sc and 0.99 for Y Nagase and Kobayashi suggest that the formal charge distribution rather is Sc²⁺C²⁻₈₂.

In a recent publication Nagase and Kobayashi (1994) compared Ce_@C₈₂ to the lighter homologues R_@C₈₂ (R = Sc, Y, La). The spin-unrestricted Hartree–Fock (UHF) method with basis sets of approximately valence double-zeta quality was applied for the fixed cage geometry mentioned above. The Ce atom was approximated with the quasirelativistic effective-core potential of Cundari and Stevens (1993) and spin–orbit coupling has been neglected. As for the other R_@C₈₂ systems previously investigated the cerium compound is significantly stabilized (40 kcal/mol), when the metal atom moves off the center (1.3 Å). Ce_@C₈₂ was found to have a closed-shell electronic ground state configuration in agreement with the experimental evidence that the compound is EPR silent. The Mulliken charge on Ce is calculated to be +1.81, i.e. formally a Ce²⁺C²⁻₈₂ charge distribution is to be assumed similar to the Sc and Y homologues. The populations of the Ce 4f and 5d orbitals are 1.38 and 0.90, respectively. The results were essentially shown to be stable with respect to an extension of the cerium basis set.

Nagase and Kobayashi (1994) also performed spin-polarized non-local densityfunctional calculations in the self-consistent Kohn–Sham formalism (Kohn and Sham 1965) using the gradient corrections by Becke (1988) for the exchange functional and by Perdew (1986) for the correlation functional. Values for electron affinities and ionization potentials for R@C₈₂ (R=Sc, Y, La, Ce) and C_n (n=60, 70, 76, 82) were calculated. For C₆₀ the theoretical and experimental values agree within 0.2 eV for both the electron affinity and the ionization potential. No experimental information is available for the other systems.

Preliminary studies on LuC₈₂ again lead to a formal decription as $Lu^{2+}C_{82}^{2-}$ (Nagase and Kobayashi 1994). This may suggest that rare earths are mostly in the +2 oxidation state in the R@C₈₂ molecules, probably with the exception of La@C₈₂ where the metal has an oxidation state of +3.

3.3.6. Hydrated lanthanide ions

Kobayashi et al. (1987) carried out self-consistent-charge discrete-variational X_{α} molecular orbital calculations (Rosén et al. 1976) for the hydrated Ce³⁺ ion, i.e. [Ce(H₂O)₉]³⁺

in the D_{3h} point group. The complex has the structure of a tricapped trigonal prism. The ground state arises from a 4f¹ configuration on the Ce³⁺ ion, whereas 5d¹ corresponds to the lowest excited configuration. A contraction of the 4f orbitals and an expansion of the 5d orbitals compared to the free Ce^{3+} ion have been observed in the complex. The $4f^1$ ground-state configuration is found to be almost exclusively split by spin-orbit interaction into atomic-like ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ ion states ($\Delta E = \frac{7}{2} \times \zeta(4f)$, $\zeta(4f) = 600 \text{ cm}^{-1}$) and to a lesser extent by the ligand field yielding seven sublevels $(3 \times E_{1/2}, 2 \times E_{3/2} \text{ and } 2 \times E_{5/2})$. For the 5d¹ excited configuration the ligand field splitting into the three components $^{2}A'_{1}$, $^{2}E'$ and $^{2}E''$ is found to dominate over spin-orbit interaction ($\Delta E = \frac{5}{2} \times \zeta(5d)$, $\xi(5d) = 1100 \text{ cm}^{-1}$) which further splits the three sublevels into five Kramers doublets $(2 \times E_{1/2}, 2 \times E_{3/2})$ and $1 \times E_{5/2}$. Experimentally five absorption and two emission bands are observed. The absorption bands may be assigned to the transitions from the ${}^{2}F_{5/2}$ ground state to the five sublevels arising from the 5d¹ excited configuration, whereas the emission bands are due to transitions from the lowest sublevel of the 5d¹ configuration to the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ states. The spin-orbit averaged $4f \rightarrow 5d$ excitation energies $(40\,600\,\text{cm}^{-1}, 42\,500\,\text{cm}^{-1}, 48\,000\,\text{cm}^{-1})$ derived by Kobayashi et al. (1987) using the transition state procedure are in excellent agreement with experimental data (39200 cm^{-1}) . 43700 cm^{-1} , 48800 cm^{-1}), despite the fact that relativistic effects have not been included in the calculation. The authors therefore performed relativistic Dirac-Hartree-Fock-Slater calculations on the free Ce³⁺ ion in order to get estimates for relativistic contributions. From their data we calculate that the spin-orbit averaged ${}^{2}F \rightarrow {}^{2}D$ excitation energy is reduced from 43 110 cm⁻¹ to 30 597 cm⁻¹ by relativistic effects. Moreover, the latter value changed to $52\,339\,\mathrm{cm}^{-1}$ when the parameter α was taken to be 1.0 instead of 0.7 as used in the nonrelativistic work. The corresponding experimental value is 49943 cm^{-1} (Martin et al. 1978). It is obvious from these data that for the nonrelativistic molecular results the good agreement with experiment is more or less accidental.

Kotzian et al. (1991) and Kotzian and Rösch (1992) applied their INDO/1 and INDO/S-CI methods to hydrated cerium(III), i.e. model complexes $[Ce(H_2O)_n]^{3+}$ (n=8,9), in order to rationalize the electronic structure and the electronic spectrum of these species. Besides the scalar relativistic effects spin–orbit coupling was also included in the INDO/S-CI studies. The spin–orbit splitting of the 4f¹ ²F and 5d¹ ²D states of the free Ce³⁺ ion was calculated as 2175 cm⁻¹ and 2320 cm⁻¹ in excellent agreement with the experimental values of 2253 cm⁻¹ and 2489 cm⁻¹, respectively. The calculated energy separation between the ²F and ²D states of approximately 44 000 cm⁻¹ (estimated from fig. 5 in Kotzian and Rösch 1992) is somewhat lower than the experimental value of 49 943 cm⁻¹ (Martin et al. 1978).

A hypothetical $[Ce(H_2O)_1]^{3+}$ model complex (C_{2v}) was considered to study metalligand interaction. The 4f orbitals on cerium were found to remain almost pure atomic orbitals in the complex and the Mulliken population analysis yielded a nearly integral occupation number of 1.01 electrons. The bonding of H₂O to the Ce³⁺ ion was found to result for about 75% from a charge donation of the water lone pairs (2a₁, 1b₂) and a H–O bonding orbital (1b₁) to the cerium 5d_{z²} (σ), 5d_{xz} and 5d_{yz} (π) orbitals. The other 25% contribution essentially comes from the charge transfer from the water 1a₁ 702

State	Exper	imental	INDO/S-CI calculations					
	crystal	solution	Kotzian et al. (1991)	Kotzian and Rösch (1992)				
E _{1/2}	39060	39630	40228	40070				
E _{3/2}	41950	41970	42933	42870				
E _{5/2}	44740	45330	45670	45940				
E _{1/2}	47400	47620	48665	48820				
E _{3/2}	50130	50000	50917	51000				

Table 39

Excited state energies (band maxima) for the experimental and calculated $4f \rightarrow 5d$ spectra of $[Ce(H_2O)_q]^{3+a}$

^a Data from Kotzian et al. (1991) and Kotzian and Rösch (1992).

All values are given in cm^{-1} .

orbital into the cerium $6p_z$ orbital. (The numbering of the orbitals starts with the valence orbitals.)

For the structure of the enneahydrated complex a tricapped trigonal prism (D_{3h}) was assumed. It is experimentally observed that all trivalent lanthanide ions can exist as enneahydrates with this structure in the solid state with trichlorosulfonate, ethylsulfate or bromate counterions. For the octahydrated complex a dodecahedron (D_{2d}) and a quadratic antiprism (D_{4d}) are the dominant experimentally observed structures. Besides these a cube (D_{4h}) and a bicapped trigonal prism $(C_{2\nu})$ were also considered. INDO/1 calculations were performed to obtain estimates for some of the structural data. The electronic states arising from the ground $4f^1$ and excited $5d^1$ superconfigurations were calculated using the INDO/S-CI method. The calculations showed that the five strong $4f \rightarrow 5d$ bands observed experimentally in the region below 50000 cm^{-1} cannot be explained when octahydrated structures are assumed. The experimentally observed spectrum however may be quite accurately reproduced when a tricapped trigonal prismatic structure, i.e. an enneahydrated complex, is assumed. All excitations from the ${}^{2}F_{5/2}$ derived molecular states were taken into account and weighted with a Boltzmann factor for room temperature. Further a common Gaussian broadening of the lines of $900 \,\mathrm{cm}^{-1}$ has been assumed. An additional experimentally observed broad band at an energy of $34\,000\,\mathrm{cm}^{-1}$ was explained to be caused by two of the octahydrated structures, i.e. the dodecahedron and the bicapped trigonal prism with lowest transition energies of 34640 cm⁻¹ and 36120 cm⁻¹, respectively. The calculated INDO/S-CI term energies are compared to experimental band maxima for the crystal and the aqueous solution in table 39. For further details and a discussion of the experimental work we refer to the original papers by Kotzian et al. (1991) and Kotzian and Rösch (1992).

Kotzian (1991) and Kotzian et al. (1995) reported INDO/S-CI results for transition energies and relative oscillator strengths of the $4f \rightarrow 4f$ excitations in the $[R(H_2O)_n]^{3+}$ (R=Pr, Nd, Tm, n=8, 9) complexes. These excitations are parity-forbidden for the free ion (Laporte selection rule), but may gain intensity due to admixture of opposite-parity character in a non-centrosymmetric environment. The field of the water ligands leads only to a small perturbation of the free ion energy levels (Pr³⁺ 4f², Nd³⁺ 4f³, Tm³⁺ 4f¹²). Due to the weak ligand-metal interaction it was not possible to infer details concerning the geometry of the complexes. Since electron-electron repulsion is found to dominate spin-orbit interaction the electronic states may best be classified using the Russell-Saunders coupling scheme. With regard to the excitation energies the calculated spectra are in excellent agreement with experimental data, however the oscillator strengths are about one order of magnitude too small. Various sources of error have been discussed, e.g. the absence of $4f^n \rightarrow 4f^{n-1}5d^1$ and ligand-to-metal charge-transfer excitations from the CI expansion or the neglect of intensity borrowing from vibrational modes. Nevertheless, the INDO/S-CI method seems to be a reliable alternative to the LFT based approaches for the interpretation of these spectra.

3.3.7. Miscellaneous polyatomics

The mechanism of H–H and C–H bond activation reactions catalyzed by the d^0 species $(cp)_2LuX$ (X=H, CH₃) has been investigated by Rabaâ et al. (1986) using the EHT method. In some calculations Lu was substituted by Sm. There are hints to a 4f-orbital participation during the reaction for the Sm complex whereas the 4f shell was found to be nonbonding for the Lu compound.

Xu and Ren (1986) performed unrestricted INDO calculations for the dimer of $bis(\eta^5$ cyclopentadienyl)ytterbium(III) methyl and discussed the charge distribution as well as the orbital energies. The compound may be viewed as two fragments of $bis(\eta^5$ cyclopentadienyl)ytterbium(III) connected by two bridging methyl groups. A Mulliken population analysis indicated that the 4f orbitals on each Yb are occupied by 13 electrons and are localized almost completely on the metal. The contributions to covalent bonding come from the Yb 5d and to a lesser extent from the Yb 6s and 6p orbitals. The authors also give the charge on the lanthanide metal as well as the Mulliken bond order for twelve mostly organometallic complexes of various lanthanide metals, but do not report details of these calculations. With respect to covalency and contribution of specific orbitals to chemical bonding similar conclusions have been drawn as for the binuclear Yb compound.

Culberson et al. (1987) report results of an INDO/1 geometry optimization for the $Ce(NO_3)_6^{2-}$ complex which are in excellent agreement with the experimental X-ray crystal structure. In this complex Ce has an unusual twelve-fold coordination (T_h point group) and a 4f occupation number of 0.46, indicating some 4f covalency. In addition large 5d (1.67), 6s (0.23) and 6p (0.33) occupations have been found for this formally Ce(IV) compound.

The CNDO method was used by Jia (1987) to investigate the structures of all lanthanide monocarbonyls and the mono- through hexacarbonyls of Nd. The 4f orbitals were not explicitly included in the calculations, an approximation which was checked by quasirelativistic EHT calculations with an explicit treatment of the 4f shell.

Jahns et al. (1992) investigated the possibility of an agostic interaction in two paradimetallated σ -phenylene complexes [((cp*)_2R)_2C_6H_4] for R=Sc and Lu using the INDO/1 method. The crystal structure of these binuclear complexes is known. They contain a bridging phenylene moiety between the two (cp*)₂R fragments. The lutetium compound exhibits unusual features, whereas the scandium compound does not. The phenylene moiety between the two Lu atoms is neither in a head-on (pure σ bonding) nor side-on (pure π bonding) position, but rather tilted by 32° out of the plane defined by the centroids of the two cyclopentadienyl ligands and the α carbon atom. As a consequence, the R-C_{α}-C_{β} angles are 118° and 88° for the Sc and Lu complexes, respectively. Jahns et al. studied the corresponding mononuclear complexes $[(cp^*)_2RC_6H_5]$. Idealized geometries were used, except for the R-C $_{\alpha}$ -C $_{\beta}$ angle which was optimized. The total energy curves showed minima at about 120° and 80° for Sc and Lu, respectively, in good agreement with the experimental values. Obviously, an agostic interaction between the metal atom and the C_6-H_6 bond is present in the lutetium complex, whereas the scandium compound shows a normal bonding between the metal and the α carbon atom. Jahns et al, found that it was not possible to explain the difference between the two rare-earth compounds by means of molecular orbitals or Walsh-type arguments. Therefore they used a partitioning of the INDO total energy in one-center (atomic) and two-center (interaction) terms which was first suggested by Pople et al. (1965), i.e.

$$E = \sum_{\lambda} E_{\lambda} + \sum_{\lambda < \mu} E_{\lambda\mu}, \tag{56}$$

where λ and μ denote atom indices. It was found that the interaction terms $E_{\lambda\mu}$ exhibit the same characteristics as the total energy with respect to a variation of the R-C_{α}-C_{β} bond angle. An analysis of these terms for the atom pairs in the agostic region showed that indeed an agostic interaction is present for Lu. The decisive difference between Sc and Lu was found by Jahns et al. to result from the different radial extent of the metal d orbitals, i.e. 1.691 a.u. (Sc) and 2.738 a.u. (Lu) are obtained for the 3d and 5d $\langle r \rangle$ expectation values from quasirelativistic Wood–Boring calculations for the atomic ground states.

The H–H activation by a Cl₂RH (R=Sc, Y, La, Lu) catalyst was studied by Cundari et al. (1993) using quasirelativistic effective core potentials at the SCF/MP2/CISD and MCSCF/SOCI levels of theory. A single-determinant wavefunction was found to be sufficient for a qualitatively correct description of the reactants, products and also transition states. A four-center (R–H₃) transition state with C_{2v} symmetry and a slightly bent H₃ moiety (bond angle around 150°) was found. The SCF and MP2 activation energies represent the upper and lower limits, respectively, for the values derived with the other methods. The relative transition state barrier height Sc \approx Y > La > Lu seems to be independent of the computational method, e.g. 34, 35, 30 and 11 kJ/mol are the MP2 results for the largest basis set.

Andrade et al. (1994) developed a so-called 'sparkle model' for Eu^{3+} ions in quantumchemical calculations using the semiempirical Austin Model 1 (AM1) method (Dewar et al. 1985). In comparison to the related modified neglect of differential overlap method (MNDO) (Dewar and Thiel 1977a,b) the AM1 method uses a modified corecore repulsion function and is therefore able to reproduce hydrogen bonds. The 'sparkle model' is based on the a priori assumption that the interaction of the metal ion with the ligand is of purely electrostatical nature and that the lanthanide 4f orbitals do not take part in chemical bonding. Eu³⁺ is treated as an integer charge of +3 at the center of a repulsion sphere of exponential form. The heat of formation was set equal to the heat of sublimation of Eu plus the sum of its first three ionization potentials. Eu³⁺ itself is assumed to have a zero ionization potential and no orbitals. The exponential parameter of the repulsion sphere and a free parameter in the core-core repulsion have been derived from a fit to the crystallographically determined geometry of [Eu(acac)₃0phen] (acac = acetylacetonate; o-phen = 1,10-phenantroline). The coordination polyhedron may be viewed as a distorted square antiprism or a distorted bicapped trigonal prism. The 24 distances, among them six Eu-O and two Eu-N bond lengths, which define the geometry of the reference compound have been reproduced in the calculations with the final set of parameters with an average deviation of 0.13 Å, the individual errors ranging from 0.01 Å to 0.30 Å. Bond angles have not been used to determine the parameters. The authors gave, as a warning not to use their model for cases with small inorganic ligands where f orbitals play an important role, the results for EuCl₃: as expected from an electrostatic model the molecule is obtained planar with a bond length of only 2.03 Å, instead of the experimentally correct pyramidal geometry and a bond length of about 2.50 Å. The authors recently tested their 'sparkle model' for a complex of a ninefold-coordinated Eu^{3+} ion, i.e. the tris(dipivaloylmethanato)(2,2':6',2''terpyridine)europium(III) complex (Andrade et al. 1995). The bond lengths and bond angles in the coordination polyhedron, a distorted tricapped trigonal prism with three N and six O atoms, have been determined from the crystal structure and were reproduced by the model with an average deviation of 0.12 Å and 5°, respectively. It appears that the parameters derived for [Eu(acac)₃o-phen] are transferable to other organometallic complexes of the Eu³⁺ ion without significant loss of accuracy.

The Gd₁₀C₄Cl₁₈ cluster was investigated by Xu and Ren (1987) using the unresticted INDO method. No metal-metal bonds have been found and the compound is stabilized by Gd–Cl–Gd and Gd–C–Gd bridging bonds. Quite a number of studies on lanthanide compounds have been published in Chinese journals; these are also listed in tables 1 and 45. Brief summaries are available from Chemical Abstracts (CA) and the citations given here include the CA registration number. Various compounds of 'chemical interest' have been studied by the unrestricted INDO (Ren et al. 1983, Li et al. 1986a,c, 1987b, Huang et al. 1991, Dong et al. 1992, Lan and Li 1992) and the X_{α} MS (Min 1992a,b) method. An EHT program for f elements has also been described (Cao et al. 1986). Since details of these studies were not available for us we do not review them here.

3.4. Solids

In this brief section on solids we will only consider molecular quantum-chemical calculations on clusters that serve as models for segments of crystals. We will not review band-structure or related calculations. This means that we will deal primarily with local phenomena related to lanthanide ions embedded in crystals. The calculations are

meaningful due to the almost core-like character of the 4f shell, at least for the heavier lanthanide atoms.

Weber et al. (1977a,b) applied the nonrelativistic multiple scattering (MS) X_{α} method to study satellite excitations in the 3d photoelectron spectra of clusters RF₃ (R = La, Ce, Pr, Nd, Yb), LaBr₃, LaO₄⁵⁻ and CeF₃⁺. For the charged species the stabilizing electrostatic field of the crystalline environment was taken into account by use of a Watson sphere bearing a charge opposite to that of the cluster. The calculations qualitatively explain the experimentally observed phenomenon which is due to an interatomic shake-up process taking place during ionization, an electron being transferred from the ligands to the R 4f shell. However, the authors state that more sophisticated calculations are required for an accurate prediction of the energetic positions and the intensities of the 3d photoelectron satellites.

Li et al. (1983) investigated the clusters RF_8^{5-} (R = Ce, Nd, Gd, Tb, Yb) embedded in a CaF₂ matrix using their intermediate neglect of differential overlap (INDO) method. The covalent contributions to chemical bonding result from the F 2p orbitals as well as the R 5d orbitals, to a lesser extent from the R 6s and 6p orbitals. The 4f orbitals do almost not take part in chemical bonding, however the authors give as a mechanism of the paramagnetic shift of the NMR spectra the polarisation of the R 5d orbitals by the R 4f orbitals which are only partially occupied. Although more spin density is transferred to the F 2p orbitals than to the F 2s orbitals, the latter contribute by roughly a factor of 30 more to the hyperfine constant.

Case and Lopez (1984) applied the Dirac–Hartree–Fock–Slater scattered-wave (DHFS-SW) (or multiple-scattering, DHFS-MS) method (Case 1982, Yang 1983) to the problem of an Yb³⁺ impurity in KMgF₃ and CaF₂ crystals to investigate spin–orbit, ligand field, Zeeman and hyperfine interactions. The authors used the YbF₆³⁻ and YbF₈⁵⁻ clusters of cubic symmetry as model systems, the influence of the rest of the lattice as well as lattice relaxation upon substitution of Mg²⁺ or Ca²⁺ by Yb³⁺ was neglected. The calculations predict Γ_6 and Γ_7 ground states arising from a hole in the highest ligand field level of the Yb 4f_{7/2} subshell. The experimentally observed spin–orbit splittings of the 4f shell are reproduced by the calculations within 8%, however the crystal-field splittings are overestimated by a factor of 1.5 to 2.5. The authors obtained good agreement with experimental values (errors of 5% or less) for the molecular g tensors and the Yb hyperfine tensors, although spin-polarisation effects have been neglected. The significant overestimate of spin transfer to the ligands was a disappointing result which, according to Case and Lopez, might question the usefulness of the DHFS-SW method for such studies. The problems might of course also be due to the limited cluster size.

Visser et al. (1992b) presented results of molecular relativistic DHFR (Dirac-Hartree– Fock–Roothaan) calculations followed by COSCI (complete open-shell configuration interaction) calculations on an Eu^{3+} impurity in a Ba_2GdNbO_6 crystal. The DHFR calculations have been performed for an average of a nonrelativistic configuration with a $4f^6$ subconfiguration on Eu^{3+} whereas the energies of the individual levels were obtained by the subsequent COSCI calculations. The Dirac–Coulomb Hamiltonian was used, i.e. the Breit interaction has been neglected. The calculations have been carried out with the program system of the Groningen group (Visser et al. 1992b, DeJong et al. 1994). The authors used medium-sized kinetically balanced basis sets without polarisation functions. Corresponding nonrelativistic calculations were also performed. This recent work may be viewed as a continuation of older nonrelativistic calculations for the same system by Van Piggelen (1978, 1980).

The Ba₂GdNbO₆ crystal has an ordered perovskite structure. The authors assumed it to be purely ionic, i.e. $(Ba^{2+})_2Gd^{3+}Nb^{5+}(O^{2-})_6$. The Eu³⁺ impurity occupies one of the Gd^{3+} sites and is surrounded by six O^{2-} ions forming an octahedron. The use of the resulting O_h symmetry was essential to make the quantum-chemical calculations feasible, i.e. the number of two-electron integrals that had to be calculated could be reduced from 15×10^9 to 254×10^6 . For details concerning, e.g., the different thresholds used for the integral evaluation we refer the reader to the original paper. In order to analyse the Eu³⁺ impurity states arising from the 4f⁶ configuration on Eu in the crystal the authors used as models a bare Eu^{3+} ion or an EuO_6^{9-} cluster embedded in a Madelung potential (MP) representing the rest of the crystal. The MP has been calculated in the cluster region by assuming an infinite purely ionic crystal. After subtracting out the electrostatic contributions of the system explicitly treated in the quantum-chemical calculations, i.e. Eu^{3+} or EuO_6^{9-} , the remaining potential was fitted with a set of point charges. The corresponding systems without MP were also considered for comparison. The authors emphasize that it is necessary to use the embedded cluster model to get a reasonable description of the crystal-field splittings of the states and that it is also essential to use relativistic orbitals. This is obvious from the one-particle energies of the 4f shell: the nonrelativistic 4f orbitals of Eu³⁺ are split by the pure electrostatic ligand field of O_h symmetry into the a_{2u} (0 cm⁻¹), t_{2u} (461 cm⁻¹) and t_{1u} (922 cm⁻¹) levels, whereas spinorbit interaction causes a considerably larger splitting of the relativistic free Eu³⁺ ion 4f shell into $4f_{5/2}$ (0 cm⁻¹) and $4f_{7/2}$ (5290 cm⁻¹) levels. The relativistic levels are further split by the ligand field yielding two groups of levels in O_h^{*} double group symmetry, i.e. e_{2u} (0 cm⁻¹), f_u (575 cm⁻¹), e_{2u} (5224 cm⁻¹), f_u (5742 cm⁻¹) and e_{1u} (6082 cm⁻¹). The one-particle energies associated with the Eu³⁺ 4f shell are changed by less than 200 cm⁻¹ when the EuO_6^{9-} cluster in the MP is considered instead.

Since the Eu 4f shell retains an atomic-like character also in the crystal environment, the Eu³⁺ impurity states may be approximately classified using the atomic symmetry labels. The results of the DHFR/COSCI calculations for the lowest states are summarized in table 40. From the high density of states (fig. 18) it is clear that individual calculations for the states resulting from the 4f⁶ configuration are currently prohibitive from a computational point of view. The dominant luminescence transitions in the Ba₂GdNbO₆:Eu system are basically atomic ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions. The first of these is a magnetic dipole transition experimentally observed in the spectrum, whereas the second is an induced electric dipole transition, allowed by vibronic coupling, and is further split by the reduction of symmetry. The results of the calculations by Visser et al. and by Van Piggelen are summarized together with experimental data in table 41. It is seen that the relativistic results are in slightly better agreement with the experimental values than the nonrelativistic results obtained by Van Piggelen more than

Free ion state ^b	d	Eu ³⁺	Eu ³⁺ (MP)°	EuO ₆ ^{9–} (MP) ^c	Free ion state ^b	d	Eu ³⁺	Eu ³⁺ (MP)°	EuO ₆ ⁹⁻ (MP) ^c
⁷ F ₀	1	0	0	0	⁵ D ₀	1	20567	20595	20246
⁷ F ₁	3	375	364	364	⁵ D ₁	3	22215	22239	21888
⁷ F ₂	2	1065	876	896	⁵ D ₂	3	24748	24722	24397
	3		1126	1113		2		24838	24419
⁷ F ₃	1	1962	1868	1912					
	3		2013	1962					
	3		2052	1980					
⁷ F ₄	3	3022	2840	2932					
	2		3117	3022					
	3		3218	3069					
	1		3310	3126					
⁷ F ₅	3	4192	4096	4118					
	2		4129	4129					
	3		4216	4206					
	3		4410	4236					
⁷ F ₆	2	5430	5294	5334					
	3		5323	5340					
	1		5386	5464					
	3		5720	5374					
	3		5755	5494					
	1		5788	5511					

Table 40

Energies of the lowest levels of a $4f^6$ configuration on Eu and their degeneracies (d) in the O_h crystal field

^a From Visser et al. (1992b), with modifications.

All energies are in cm⁻¹.

^b The degeneracies of the free ion states are 2J + 1.

^c MP denotes the use of a Madelung potential modeling the crystal.

a decade ago. The differences probably result from several sources of error. Although the applied Dirac-Coulomb Hamiltonian could only be improved by inclusion of the Breit or Gaunt interaction, the COSCI wavefunction essentially does not account for electron correlation effects. A direct CI scheme with which the remaining correlation errors would partly be removed has recently been developed and implemented (Visscher 1993, Visscher et al. 1993). Moreover, the description of the O²⁻ ions at the DHF level with a basis of valence double-zeta quality might certainly affect the results. Larger basis sets, however, are not feasible within this model, not only for reasons of computational effort but also since positive point charges of the MP are in the direct vicinity of the O²⁻ ions. This difficulty might be overcome by the use of relativistic PPs modeling the ions surrounding the EuO₆⁹⁻ cluster. Finally the effect of the cluster size has to be investigated further.



Fig. 18. Density of 4f⁶ ⁷F states (dos) vs. term energy (*T*) for EuO₆^{9–} embedded in a Madelung potential. Data taken from DHFR/COSCI calculations by Visser et al. (1992b).

Table 41

Transition energies of the fluorescence in the Ba₂GdNbO₆:Eu system from Dirac-Hartree-Fock-Roothaan and complete open-shell configuration interaction calculations for three model systems, in comparison with experimental data^a

Transition	Eu ³⁺ 20189	Eu ³⁺ (MP) ^b 20229	EuO ₆ ^{9–} (MP) ^b		Experiment
$5 D_0 \rightarrow 7 F_1$			19871	(20459)	16800
${}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{2}(\mathrm{E}_{\mathrm{g}})$	19507	19718	19259	(19738)	16150°
${}^{5}D_{0} \rightarrow {}^{7}F_{2} (T_{2g})$	19507	19467	19149	(19599)	16150°

^a From Visser et al. (1992b).

Values are given in cm⁻¹.

^b MP denotes the use of a Madelung potential modeling the crystal. Nonrelativistic theoretical values are given in parentheses.

^c Unweighted average over six lines observed in this region. The separation between the lines is about 100 cm⁻¹.

Results comparable in quality to those presented by Visser et al. could also be obtained by more approximate schemes of relativistic quantum chemistry. Visser et al. indeed state that their results could serve as a reference for more approximate methods. A considerable reduction in the computational effort could be obtained if a two-component all-electron scheme instead of the four-component DHFR approach would be applied: 99.2% of the two-electron integrals calculated by Visser et al. result from the presence of the lower components in the one-particle functions. In addition the computational effort for the SCF iterations and the subsequent integral transformation also would be considerably

			· ·	•	
Ion	Configuration	Orbitals	Calculation	Experiment	Error
Ce ²⁺	4f ²	4f ²	-51.615	-56.009	4.394
		4f ² , 4f ¹ 5d ¹ , 5d ²	-50.689	-56.009	5.320
	$4f^1 5d^1$	4f ² , 4f ¹ 5d ¹ , 5d ²	-52.864	-55.889	3.025
	5d ²	4f ² , 4f ¹ 5d ¹ , 5d ²	-47.086	-51.156	4.070
Ce ³⁺	4f1	4f ¹	-34.867	-36.598	1.731
	5d ¹	5d ¹	-29.492	-30.406	0.914
Ce ⁴⁺		$4f^{0}, 5d^{0}$	0.000	0.000	0.000

Table 42

Free-ion average energies of a nonrelativistic configuration relative to the energy of the Ce⁴⁺ ion from Dirac-Hartree–Fock–Roothaan calculations, in comparison with experimental data^a

^a From Visser et al. (1993), with modifications.

All energies are in eV.

reduced, whereas the relatively small effort for the actual construction and diagonalisation of the Hamiltonian matrix in the COSCI scheme would essentially remain unchanged. An accurate two-component PP scheme could even lead to further savings without significant loss of accuracy. However, the CI step certainly will become the most time-consuming part of the calculation even in four-component approaches when the short COSCI expansions are replaced by longer CI expansions which also account for dynamic electron correlation effects. For large systems these could only be avoided by use of a semiempirical method like the INDO/S-CI approach. We note that density-functional methods currently provide no alternative if information on individual electronic states is desired.

Visser et al. (1993) calculated the energy levels of cerium centers in CaF_2 , SrF_2 and BaF_2 crystals and studied cerium–electron and cerium–hole interactions in these systems using the Dirac–Hartree–Fock–Roothaan (DHFR) and complete open-shell configuration interaction (COSCI) schemes. The calculations were carried out with the code developed by the group of Nieuwpoort and coworkers in Groningen (Visser et al. 1992b). In these studies relatively large kinetically balanced basis sets without polarisation functions were applied, the nuclei were approximated as point charges and the Breit interaction was neglected. The cerium center was modeled by a CeF_8 cluster placed into a fluorite-type lattice of 406 point charges spherically distributed around the cerium center. The point charges in the two outer shells were adjusted so as to give the correct Madelung potential at the cerium and fluorine sites in the CeF_8 cluster. The effects of lattice relaxation were also taken into account.

The energy levels of the free Ce^{n+} (n=2,3,4) ions were calculated and compared to experiment (table 42). For Ce^{2+} the spinors were taken from DHFR calculations for a configurational average of either 4f² or 4f², 4f¹5d¹ and 5d². The energies of the individual states were then determined by a COSCI calculation for two electrons in the 4f or

4f and 5d orbitals, respectively. The COSCI calculations in this form essentially do not account for electron correlation effects but rather are an efficient scheme to calculate all individual states arising from a given set of configurations. For Ce^{3+} and Ce^{4+} no COSCI calculations were necessary. For Ce^{3+} the $4f^1$ or $5d^1$ average was treated in the DHFR calculations and the energies of the individual ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ or ${}^{2}D_{3/2}$ and ${}^{2}D_{5/2}$ states were derived by calculating the difference of the orbital energies from the average orbital energy. For Ce⁴⁺ the ¹S₀ ground state was considered. From the data compiled in table 42 it is clear that semiempirical corrections have to be applied for the subsequent cluster calculations if meaningful results are to be obtained. The errors in the theoretical results increase with increasing number of electrons and are of the order of a few electron volts. They mainly stem from two sources: first the one-particle basis set is large but not at the DHF limit and the spinors have been optimized for a configurational average and not for the individual states; second, and probably much more important, the many-particle basis set does not contain other configurations than those considered in the configurational average. Terms neglected in the Hamiltonian are probably of less importance. Visser et al. assumed the cerium centers in the crystal to remain essentially in their free ion states and therefore added the differences between the calculated and experimentally observed free ion levels to the corresponding levels in the embedded CeF₈ cluster.

Using the same methods as for the free cerium ions the energy levels of the $CeF_8^{(8-n)-}$ (n=2,3,4) clusters embedded in the Madelung potential (MP) were calculated. The calculated energies were corrected with the increments $\Delta E^{b,c}$ (b, basis set; c, correlation) derived from the free-ion calculations discussed above:

$$E(\operatorname{CeF}_{8}^{(8-n)-} \operatorname{MP}) = E(\operatorname{CeF}_{8}^{(8-n)-} \operatorname{MP})^{\operatorname{DHFR}} + \Delta E^{\operatorname{b,c}}(\text{free ion}).$$
(57)

It is expected that lattice relaxation is significant when an alkaline-earth ion is replaced by a cerium ion in a crystal. Visser et al. therefore considered the variation of their results with respect to changes in the cerium nearest-fluorine-neighbor distance $r(Ce-F_n)$. The authors report the somewhat surprising result that the potential energy curves of the configurational average from nonrelativistic and relativistic calculations could be brought into agreement within less than 0.1 eV over the range of $r(Ce-F_n)$ values of interest. A vertical shift accounting for relativity and differences in the one-particle basis set had to be applied for the nonrelativistic energies. Visser et al. conclude that electrons occupying the 5d, 6s and 6p orbitals can be described reasonably in a nonrelativistic way. The $r(Ce-F_n)$ dependence of the selected energy levels of the embedded cluster was therefore derived from computationally less intensive nonrelativistic calculations. The following states were considered:

- (i) $Ce^{2+} (4f^2 {}^{3}H_4) T_2$,
- (ii) the lowest Ce^{2+} ($4f^{1}5d^{1}$) T₂ state.
- (iii) $Ce^{3+} (4f^{1 \ 2}F_{5/2}) F_u$, (iv) $Ce^{3+} (5d^{1 \ 2}D_{3/2}) F_g$ and
- (v) Ce^{4+} (¹S₀) A₁.

The labels in parentheses refer to atomic configurations and states as far as these are still meaningful in the embedded crystal, the state labels refer to the O_b^{*} double point group.
Table 43
comparison between calculated energies for the Ce ³⁺ center in CaF ₂ and the experimental values ascribed to a
CeF_{nn} center ^a

Lower state	Upper state	Calcu	Experiment	
		r = 2.680 Å	r=2.435 Å	_
$(4f^{1} {}^{2}F_{5/2}) F_{u}$	$(4f^{1\ 2}F_{5/2}) E_{2u}$	224	421	579
$(4f^{1\ 2}F_{7/2}) E_{1u}$	$(4f^{1\ 2}F_{7/2}) E_{2u}$	385	725	1370
$(4f^{1} {}^{2}F_{5/2})$ avg.	$(4f^{1-2}F_{7/2})$ avg.	2253	2253	2396
(5d ¹ ² D _{3/2}) F _g	$(5d^{1-2}D_{5/2}) E_{2g}$	11842	22279	21438
$(4f^{1} {}^{2}F_{5/2}) F_{u}$	$(5d^{1-2}D_{3/2}) F_g$		43204	31932

^a From Visser et al. (1993), with modifications.

All values are in cm⁻¹.

^b The theoretical Dirac-Hartree-Fock-Roothaan and complete open-shell configuration interaction values have been corrected to agree with the experimental values for the free Ce^{3+} ion.

Calculations are for two different r, the cerium-nearest-fluorine-neighbor distance.

The calculated data were used to derive repulsive cerium–fluorine pair potentials of exponential form which were used together with the point-charge information in a polarizable ion model to determine the minimum-energy geometry of a defect in an infinite crystal. Three models for a cerium center in an alkaline-earth fluoride crystal were considered: (i) the charge-uncompensated cerium center (Ce) and a cerium center with a charge-compensating fluorine ion at (ii) the nearest-neighbor (100) interstitial site (CeF_{nn}) or (iii) the next-nearest-neighbor (111) interstitial site (CeF_{nn}). The corrections $\Delta E^{\rm lr}$ due to lattice relaxations (lr) were also added to the DHFR and COSCI results in order to obtain the energy of a cerium center in an alkaline-earth lattice, i.e.

$$E(\text{Ce center}) = E(\text{CeF}_{8}^{(8-n)-} \text{MP}) + \Delta E^{\text{lr}}.$$
(58)

Table 43 lists the corresponding relative energies with respect to the cerium center in the Ce³⁺ (4f_{5/2} ${}^{2}F_{5/2}$) F_u ground state. It is obvious from these data that lattice relaxation which accounts in some cases up to almost 3 eV has to be considered. For details of these non-quantum-chemical calculations we refer the reader to the original paper by Visser et al. (1992b) which also contains references for the applied computer program. Results for selected states of a Ce³⁺ center in CaF₂ are summarized in table 43 together with available experimental data. Quite satisfactory results are obtained for energy differences between states belonging to the same nonrelativistic configuration on cerium, however the separation between the lowest states arising from 4f¹ and 5d¹ is too large by about 1.4 eV. The authors attributed the disagreement to the small CeF₈⁽⁸⁻ⁿ⁾⁻ cluster actually treated in the quantum-chemical calculations, i.e. the possibility of an interaction between the cerium 5d and the calcium 4s and 3p states was excluded. We note here again that the quantum-chemical treatment of formally F⁻ ions in the

CaF_2 and BaF_2^*							
Cerium	Lattice	CaF ₂		BaF ₂			
configuration	geometry	Ce	CeF _{nn}	CeFnnn	Ce	CeF _{nn}	CeF _{nnn}
Ce ²⁺ 4f ²	Ce ²⁺ 4f ²	1.39	2.06	2.18	1.40	1.90	1.96
	Ce ³⁺ 4f ¹	3.47	4.03	4.21	3.60	4.06	4.19
Ce ²⁺ 4f ¹ 5d ¹	$Ce^{2+} 4f^1 5d^1$	0.99	1.58	1.75	1.33	1.80	1.92
	Ce ³⁺ 4f ¹	2.62	3.13	3.36	3.03	3.47	3.66
Ce ³⁺ 4f ¹	$Ce^{2+} 4f^2$	2.14	2.09	2.11	2.33	2.34	2.36
	$Ce^{2+} 4f^1 5d^1$	1.69	1.66	1.67	1.82	1.83	1.87
	$Ce^{3+} 4f^1$	0.00	0.00	0.00	0.00	0.00	0.00
	$Ce^{3+} 5d^1$	0.00	0.05	0.01	0.00	0.04	0.01
	Ce ⁴⁺	1.63	1.53	1.84	1.81	1.74	1.73
Ce ³⁺ 5d ¹	$Ce^{2+} 4f^2$	7.60	7.53	7.55	7.90	7.89	7.93
	$Ce^{2+} 4f^1 5d^1$	7.12	7.08	7.10	7.34	7.35	7.40
	$Ce^{3+} 4f^{1}$	5.36	5.40	5.35	5.39	5.43	5.38
	$Ce^{3+} 5d^{1}$	5.36	5.35	5.34	5.39	5.39	5.37
	Ce ⁴⁺	6.95	6.85	7.15	7.17	7.10	7.04
Ce ⁴⁺	Ce ³⁺ 4f ¹	9.21	8.78	8.64	8.57	8.24	8.12
	Ce ⁴⁺	7.44	6.95	6.90	6.58	6.15	6.21

Table 44 Energies of the lowest levels of a configuration of Ce, CeF_{nn} and CeF_{nnn} centers in the alkaline-earth fluorides CaF_n and BaF_n^a

^a From Visser et al. (1993), with modifications.

The values are relative to the $Ce^{3+} 4f^{1-2}F_{5/2}$ ground state.

All energies are given in eV.

direct vicinity of +2 point charges (or helium nuclei) modeling the alkaline-earth ions is only possible for rather limited basis sets describing the charge distribution around the fluorine centers. Given a basis set at the point charges or merely diffuse functions on fluorine, the electrons in the cluster would unphysically tend to neutralize these point charges. The application of relativistic PPs (Dolg 1995) would overcome these problems.

Given the data compiled in table 44 Visser et al. discussed electron or hole emission from cerium centers, i.e. the center stability with respect to a change of charge on the cerium ion. They only considered the effect of cold free electrons and holes, i.e. the energy of the electron was assumed to be 0 eV (bottom of the conduction band) and those of the holes $-E_g$ (top of the valence band), where the known band-gap energy E_g for the host

lattice is 12.1 eV (11.0 eV) for CaF₂ (BaF₂). Their results can be briefly summarized as follows:

- (i) due to lattice relaxations the energy levels of the charge-compensated CeF_{nn} and CeF_{nnn} centers are equal within 0.3 eV, whereas those of the charge-uncompensated Ce center differ from them by up to 0.8 eV;
- (ii) all three modeled centers are only stable against electron or hole emission if the cerium ion is in a trivalent or tetravalent state;
- (iii) if free electrons are present, the tetravalent centers are unstable and are converted into trivalent centers by electron capture;
- (iv) in qualitative agreement with experiment the charge-uncompensated cerium center in a divalent state is found to be metastable with respect to electron emission.

Visser et al. also considered electron or hole absorption by cerium centers in the Ce^{3+} ground state and conclude that it is a slow process. In brief, their results are:

- (v) cold electrons cannot be captured at trivalent cerium ions, possibly they are captured near them due to a stabilization by the positive charge;
- (vi) cold holes can be captured at trivalent cerium ions provided a considerable lattice relaxation yielding a 2-3 eV energy gain takes place; however, due to the positive charge on the cerium center the hole capture rate is probably relatively small.

The study by Visser et al. impressively demonstrates that rigorous relativistic ab initio calculations can also be applied to investigate local phenomena in solids. However, keeping in mind the multiple sources of error in the representation of the wavefunction in the study by Visser et al. it is likely that results of a comparable quality could be obtained with simplified quantum-chemical schemes, e.g. the quasirelativistic PP approach or the INDO method.

A related DHFR study on cerium centers (site symmetry given in parentheses) in inorganic scintillator crystals, i.e. BaF₂ (O_h), LaF₃ (D_{3h}), Yttrium Aluminium Perovskite (YAP) YAlO₃ (C_s) and Yttrium Aluminium Garnet (YAG) Y₃Al₅O₁₂ (D_2) has recently been published (Andriessen et al. 1994a,b). Nonrelativistic results for Lutetium Oxyorthosilicate (LSO) $Lu_2(SiO_4)O(C_1)$ were also reported. The authors investigated the $4f \rightarrow 5d$ energy separation and the overall splitting of the 4f and 5d levels due to spin-orbit coupling and the ligand field. The cerium center is modeled by a Ce^{3+} ion in a 4f¹ or 5d¹ configuration, the nearest-neighbor oxygen or fluorine anions and a Madelung potential created by several hundreds of point charges representing the electrostatic effects of the rest of the crystal. In some cases idealized structures with higher local symmetry have been used to make the calculations feasible (i.e. D_{3h} instead of D_2 for LaF₃) and lattice relaxation as well as electron correlation effects have been neglected. For LSO only the nonrelativistic work was feasible. The authors report that it was not possible to derive small basis sets for cerium, since upon the $4f \rightarrow 5d$ excitations not only the 5s and 5p, but also the 4s, 4p and 4d shells underwent a significant contraction. The corresponding transition energies are of the magnitude $20000-60000 \text{ cm}^{-1}$. The calculations reproduce the experimental values with errors in the range 100-7000 cm⁻¹. Andriessen et al. suppose that the reasonable agreement between their calculations and the available experimental

data is partly due to an error compensation, i.e. the neglect of correlation contributions (roughly 6450 cm^{-1} for the free Ce³⁺ ion) is compensated by basis-set superposition errors present in some of the calculations. Correlation is known to lower the 4f¹ with respect to the 5d¹ configuration, whereas the basis-set effect results mainly from contributions of the ligand orbitals to the cerium orbitals. In order to get convergence to 5d¹ states of cerium in Y₃Al₅O₁₂ the authors had to discard the f orbitals on cerium resulting in too high energies of the 5d¹ compared to the 4f¹ configuration. Excited cerium in LSO may well be a Ce⁴⁺ ion or at least the 5d orbitals are strongly mixed with the oxygen ligand 2s and 2p levels.

Gérard et al. (1994) used the multiple-scattering local spin-density (Vosko et al. 1980) method to investigate the clusters LaF_9^{6-} and EuF_9^{6-} as models for the LaF_3 and $Eu^{3+}:LaF_3$ solids. Relativistic effects were included using the scheme of Boring and Wood (1979a,b).

4. Conclusions

We have reviewed the state of electronic structure theory for lanthanide-containing molecules. (The present article is supposed to cover the relevant literature until the end of 1994.) The first quantum-chemical calculation on these systems was published in 1976 and until the first review written by Pyykkö in 1987 only about 30 papers appeared in the literature. Since then enormous progress, especially in the quality of methods applied, has been made as is evident from a comparison of tables 1 and 45. An efficient intermediate neglect of differential overlap scheme with parametrizations for ground and excited states was developed and complements the long-used extended Hückel approach on the side of the semiempirical methods. Some progress has also been made in the application of quasirelativistic density-functional schemes to lanthanide containing systems. Several parametrizations of pseudopotentials and effective core potentials have been derived and applied in numerous studies. In addition to these approximate ab initio methods the Dirac-Hartree-Fock-Roothaan scheme based on the Dirac-Coulomb-(Breit/Gaunt) Hamiltonian was used for studies of atoms and molecules containing a single lanthanide atom. The recent development of corresponding coupled-cluster and multi-reference configuration interaction programs gives hope that accurate ab initio calculations on small lanthanide systems will become feasible in the near future.

Many problems of course remain to be solved, especially for the all-electron and valence-only ab initio schemes. On the one hand there remains the problem of the rather large number of low-lying electronic states due to an open 4f shell, and systems with two or even more lanthanide atoms will be very difficult to treat accurately. Even if only a single 4f shell is considered and one is interested in calculating energy differences between electronic states which arise from different 4f occupations the limitations of the available computational resources and computer codes often severely affect the quality of the results. This is especially true when electron correlation and relativistic effects including spin-orbit interaction are both to be treated.

Method ^a	Molecules ^b	Reference
DHFR, CI	EuO_6^{9-} in MP	Visser et al. (1992b)
	CeF_8^{n-} in MP (n=4, 5, 6)	Visser et al. (1993)
	CeF_{8}^{5-} , CeF_{11}^{8-} , CeO_{12}^{21-} , CeO_{8}^{13-} in MP	Andriessen et al. (1994a,b)
QR-HFS	CeO ₂ , YbCl ₂	DeKock et al. (1990)
QR-DFT	Ce @ C ₂₈	Rösch et al. (1993), Häberlen et al. (1992)
	RH, RO, RF ($R = La$, Gd, Yb, Lu)	Wang and Schwarz (1995)
	RO (R=La, Eu, Gd, Yb), YbF	Wang et al. (1995)
	RF_{9}^{6-} (R = La, Eu)	Gérard et al. (1994)
	$\operatorname{CeO}_2^{q+}(q=0, 1)$	Heinemann et al. (1996)
$QR-X_{\alpha}$ SW	$(cp)_2 R (R = Sm, Yb), (cp)_3 Sm$	Min (1992a)
	$(cp)_2 YbC_2H_2$, $(cp)_2 Yb(OC)_2$	Min (1992b)
PP, CI	RH, RO, RF ($R = La - Lu$)	Dolg and Stoll (1989), Dolg et al. (1989c)
	CeO	Dolg et al. (1989a, 1991a)
	RX_3 (R = La, Eu, Gd, Yb, Lu; X = F, Cl, Br, I)	Dolg et al. (1989c)
	GdO	Dolg et al. (1990a)
	EuO	Dolg et al. (1990b)
	RAu (R = La, Lu)	Schwerdtfeger and Dolg (1991)
	RX_2 (R=Eu, Yb;X=F, Cl, Br, I)	Dolg et al. (1991b)
	RF_3 (R = La-Lu)	Dolg et al. (1991b)
	RX_3 (R = La, Eu, Gd, Yb, Lu; X = Cl, Br, I)	Dolg et al. (1991b)
	LaX_3 (X=H, F, Cl)	DiBella et al. (1993)
	RHe^{3+} (R = La, Eu, Gd, Yb, Lu)	Dolg et al. (1991c)
	$R_2 (R = La - Lu)$	Dolg et al. (1992a)
	YbH, YbF	Dolg et al. (1992b)
	YbO	Dolg et al. (1992c)
	LaNH ⁺ , La(cp)NH	Cundari (1992)
	$La(cp)_2^+$	Kaupp et al. (1992)
	$Eu(cp)_2$, $Yb(cp)_2$	Kaupp et al. (1993)
	RO ($R = Ce$, Eu, Yb), RF ($R = Ce$, Yb)	Dolg et al. (1993a)
	LaH	Das and Balasubramanian (1990)
	LaH ₂	Das and Balasubramanian (1991a)
	LaH_{n}^{+} (n = 1, 2)	Das and Balasubramanian (1991b)
	$Ce(cot)_2$	Dolg et al. (1991d, 1995)
PP, CAS	LaO, LaO ⁺	Márquez et al. (1994)
PP, PT	$La^{3+}L_3 L = NH_3, H_2O, HF$	Kaupp and Schleyer (1992)
PP, DFT	$R @ C_{60}^{q} (q = -1, 0, +1)$	Rosén and Wästberg (1988, 1989)
		continued on next page

Table 45

Method ^a	Molecules ^b	Reference
PP, RHF	$R @ C_{60}^{n+}$ (R=La, Eu; n=0, 1)	A.H.H. Chang et al. (1991)
PP, UHF	La @ C ₈₂	Nagase et al. (1993), Nagase and Kobayashi (1993)
	Ce @ C ₈₂	Nagase and Kobayashi (1994)
INDO/S-CI	PrO, TmO	Kotzian and Rösch (1991a)
	CeO	Kotzian and Rösch (1991b)
	$[R(H_2O)_{9}^{3+}]$ (R = Ce, Pr, Nd, Tm)	Kotzian (1991), Kotzian et al. (1995)
	$[Ce(H_2O)_n^{3+}]$ (n=8, 9)	Kotzian et al. (1991), Kotzian and Rösch (1992)
INDO	$[((cp^*)_2Lu)_2 C_6H_4]$	Jahns et al. (1992)
	$[(CCl_3CO_2)_3R(phen)C_2H_5OH]_2$ (R = Pr, Sm)	Dong et al. (1992)
	$[Ce(CO_3)_3 O_2]_2^{8-}$	Lan and Li (1992)
CNDO	RCO (R=La-Lu), Nd(CO) _n (n=1, 6)	Jia (1987)
AMI	Eu(acac) ₃ o-phen	Andrade et al. (1994)
	Eu(dpm), terpy	Andrade et al. (1995)

Table 45, continued

^a Methods:	^b Abbreviations:
AM1, Austin method 1;	cp, cyclopentadiene C_5H_5 ;
CAS, complete active space (multiconfiguration	cot, cyclooctatetraene C ₈ H ₈ ;
self-consistent field);	acac, acetylacetonate;
CI, configuration interaction;	o-phen, 1,10-phenantroline;
CNDO, complete neglect of differential overlap;	phen, phenantroline;
DFT, density-functional theory;	dpm, dipivaloylmethanate;
DHFR, Dirac-Hartree-Fock-Roothaan;	terpy, 2,2':6',2"-terpyridine.
HFS, Hartree–Fock–Slater;	
INDO, intermediate neglect of differential overlap;	
INDO/S-CI, INDO adapted for spectroscopy and	
spin-orbit CI;	
MP, Madelung potential;	
PP, pseudopotential;	
PT, perturbation theory;	
RHF, restricted Hartree-Fock;	
SW, scattered wave;	
UHF, unrestricted Hartree-Fock;	
QR, quasirelativistic.	

Acknowledgements

The authors are grateful to P. Fulde and H. Preuß for their interest and support in their work on f element systems. We want to thank P. Pyykkö and W.H.E. Schwarz for critically reading parts of the manuscript and for valuable discussions. Thanks are due to

K. Balasubramanian for sending us a preprint of his review article in this Handbook and to the following scientists who communicated their results prior to publication or provided preprints: H. Cornehl, J.-C. Krupa, T. Cundari, C. Heinemann, U. Kaldor, W. Küchle, H. Merenga, W.C. Nieuwpoort, R.M. Pitzer, N. Rösch, W.H.E. Schwarz, P. Schwerdtfeger, and W.J. Stevens.

M.D. thanks R.M. Pitzer for his hospitality during two stays at the Ohio State University. The computer time granted by the Ohio Supercomputer Center and the financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged. Last but not least M.D. thanks A. Nicklass for useful hints concerning $\[mathbb{LT}_EX$ during the preparation of the manuscript.

Note added in proof

Results of quasirelativistic pseudopotential calculations at the unrestricted Hartree–Fock and multiconfiguration self-consistent field level for the equilibrium geometries of the lanthanide trihalides RX_3 (X=F, Cl, Br, I) have been presented by Cundari et al. (1995). Kobayashi et al. (1995) report Hartree–Fock and density-functional calculations of La₂@C₈₀.

References

- Ackermann, R.J., E.G. Rauh and R.J. Thorn, 1976, J. Chem. Phys. 65, 1027.
- Aerts, P.J.C., 1986, Towards relativistic quantum chemistry, Thesis (University of Groningen, Netherlands).
- Aerts, P.J.C., and W.C. Nieuwpoort, 1986a, Phys. Scripta 36, 433.
- Aerts, P.J.C., and W.C. Nieuwpoort, 1986b, Int. J. Quantum Chem. Symp. 19, 267.
- Almloef, J., K. Faegri and H.H. Grelland, 1985, Chem. Phys. Lett. **114**, 53.
- Ames, L.L., P.N. Walsh and D. White, 1967, J. Phys. Chem. 71, 2707.
- Andrade, A.V.M., N.B. da Costa Jr, A.M. Simas and G.F. de Sá, 1994, Chem. Phys. Lett. **227**, 349.
- Andrade, A.V.M., N.B. da Costa Jr, A.M. Simas and G.F. de Sá, 1995, J. Alloys & Compounds 225, 55.
- Andrae, D., U. Häußermann, M. Dolg and H. Preuß, 1990, Theor. Chim. Acta 77, 123.
- Andriessen, J., P. Dorenbos and C.W.E. van Eijk, 1994a, Mater. Res. Soc. Symp. Proc. 348, 355.
- Andriessen, J., H. Merenga, P. Dorenbos and C.W.E. van Eijk, 1994b, in: New Challenges in

Computational Quantum Chemistry, eds R. Broer, P.J.C. Aerts and P.S. Bagus (Department of Chemical Sciences and Material Science Centre, University of Groningen, Netherlands).

- Bachelet, G.B., and M. Schlüter, 1982, Phys. Rev. B 25, 2103.
- Bachelet, G.B., D.R. Hamann and M. Schlüter, 1982, Phys. Rev. B 26, 4199.
- Baeck, K.K., and Y.S. Lee, 1994, J. Chem. Phys. 100, 2888.
- Baerends, E.J., W.H.E. Schwarz, P. Schwerdtfeger and J.G. Snijders, 1990, J. Phys. B 23, 3225.
- Bagus, P.S., Y.S. Lee and K.S. Pitzer, 1975, Chem. Phys. Lett. 33, 408.
- Balasubramanian, K., 1989, J. Phys. Chem. 93, 6585.
- Balasubramanian, K., 1994, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 18, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam) p. 29.
- Balasubramanian, K., and K.S. Pitzer, 1987, in: Ab Initio Methods in Quantum Chemistry, Vol. 1, ed. K.P. Lawley (Wiley, New York) p. 287.

- Barandiarán, Z., and L. Seijo, 1992, Can. J. Chem. 70, 409.
- Barandiarán, Z., and L. Seijo, 1994, J. Chem. Phys. 101, 4049.
- Barandiarán, Z., L. Seijo and S. Huzinaga, 1990, J. Chem. Phys. 93, 5843.
- Bardsley, J.N., 1974, Pseudopotentials in atomic and molecular physics, in: Case Studies in Atomic Physics, Vol. 4, eds M.R.C. McDowell and E.W. McDaniel (North-Holland, Amsterdam) p. 299.
- Barrow, R.F., and A.H. Chojinicki, 1975, Trans. Faraday Soc. II 71, 728.
- Barthelat, J.C., M. Pélissier and P. Durand, 1980, Phys. Rev. A 21, 1773.
- Beattie, I.R., J.S. Ogden and R.S. Wyatt, 1983, J. Chem. Soc., Dalton Trans., p. 2343.
- Becke, A.D., 1988, Phys. Rev A 38, 3098.
- Bender, C.F., and E.R. Davidson, 1980, J. Inorg. Nucl. Chem. 42, 721.
- Berg, R.A., L. Wharton, W. Klemperer, A. Bucheler and J.L. Stauffer, 1965, J. Chem. Phys. 43, 2416.
- Bergner, A., M. Dolg, W. Küchle, H. Stoll and H. Preuß, 1993, Mol. Phys. 80, 1431.
- Bernard, A., and C. Effantin, 1986, Can. J. Phys. 64, 246.
- Bernard, A., and A.M. Sibai, 1980, Z. Naturf. 35a, 1313.
- Bethe, H.A., and E.E. Salpeter, 1957, Quantum Mechanics of One- And Two-Electron Atoms (Springer, Berlin).
- Blaise, J., and J.-F. Wyart, 1992, Niveaux d'Energie et Spectres Atomiques des Actinides, Tables Internationales de Constants Selectionnées Vol. 20 (Centre National de la Recherche Scientifique, Paris).
- Blume, M., and R.E. Watson, 1962, Proc. R. Soc. A 270, 127.
- Blume, M., and R.E. Watson, 1963, Proc. R. Soc. A 271, 565.
- Boerrigter, P.M., E.J. Baerends and J.G. Snijders, 1988, Chem. Phys. 122, 357.
- Bonifacic, V., and S. Huzinaga, 1974, J. Chem. Phys. 60, 2779.
- Boring, A.M., and J.H. Wood, 1979a, J. Chem. Phys. 71, 32.
- Boring, A.M., and J.H. Wood, 1979b, J. Chem. Phys. 71, 392.
- Born, M., and J.R. Oppenheimer, 1927, Ann. Phys. 84, 457.

- Boudreaux, E.A., and E. Baxter, 1994, Int. J. Quantum Chem. Symp. 28, 565.
- Breit, G., 1929, Phys. Rev. 34, 553.
- Breit, G., 1930, Phys. Rev. 36, 383.
- Breit, G., 1932, Phys. Rev. 39, 616.
- Breit, G., 1938, Phys. Rev. 53, 153.
- Broer, R., P.J.C. Aerts and P.S. Bagus, eds, 1994, New Challenges in Computational Quantum Chemistry (Department of Chemical Sciences and Material Science Centre, University of Groningen, Netherlands).
- Brown, G.E., and D.G. Ravenhall, 1951, Proc. R. Soc. A 208, 552.
- Cai, Z., V. Meiser Umar and C. Froese Fischer, 1992, Phys. Rev. Lett. 68, 297.
- Cao, Y., G. Cao and M. Li, 1986, Jisuanji Yu Yingyong Huaxue **3**, 219. (CA 106: 90391.).
- Car, R., and M. Parrinello, 1985, Phys. Rev. Lett. 55, 2471.
- Carette, P., 1990, J. Mol. Spectrosc. 140, 269.
- Carette, P., and A. Hocquet, 1988, J. Mol. Spectrosc. 131, 301.
- Carette, P., A. Hocquet, M. Douay and B. Pinchemel, 1987, J. Mol. Spectrosc. 124, 243.
- Case, D.A., 1982, Annu. Rev. Phys. Chem. 33, 151.
- Case, D.A., and J.P. Lopez, 1984, J. Chem. Phys. 80, 3270.
- Chai, Y., T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford and R.E. Smalley, 1991, J. Chem. Phys. 95, 7564.
- Chandra, P., and B.A. Hess, 1994, Theor. Chim. Acta 88, 183.
- Chang, A.H.H., and R.M. Pitzer, 1989, J. Am. Chem. Soc. 111, 2500.
- Chang, A.H.H., W.C. Ermler and R.M. Pitzer, 1991, J. Chem. Phys. 94, 5004.
- Chang, A.H.H., K. Zhao, W.C. Ermler and R.M. Pitzer, 1994, J. Alloys and Compounds **213/214**, 191.
- Chang, C., M. Pélissier and P. Durand, 1986, Phys. Scripta 34, 394.
- Chang, T.-C., P. Habitz, B. Pittel and W.H.E. Schwarz, 1974, Theor. Chim. Acta 34, 263.
- Chang, T.-C., P. Habitz and W.H.E. Schwarz, 1977, Theor. Chim. Acta 44, 61.
- Christiansen, P.A., 1986, Chem. Phys. Lett. 127, 50.
- Christiansen, P.A., and K.S. Pitzer, 1980, J. Chem. Phys. 73, 5160.
- Christiansen, P.A., Y.S. Lee and K.S. Pitzer, 1979, J. Chem. Phys. **71**, 4445.
- Christiansen, P.A., K. Balasubramanian and K.S. Pitzer, 1982, J. Chem. Phys. 76, 5087.

- Christiansen, P.A., W.C. Ermler and K.S. Pitzer, 1985, Annu. Rev. Phys. Chem. 36, 407.
- Clack, D.W., and K.D. Warren, 1976, J. Organomet. Chem. 122, C28.
- Cohen, E.R., and B.N. Taylor, 1987, Phys. Today 40, 11.
- Connor, J.A., 1986, in: Metal Clusters in Catalysis, Studies in Surface Science and Catalysis, Vol. 29, eds B.A. Gates, L. Guczi and H. Knoezinger (Elsevier, Amsterdam).
- Cory, M.G., S. Köstlmeier, M. Kotzian, N. Rösch and M.C. Zerner, 1994, J. Chem. Phys. 100, 1353.
- Cosmovici, C.B., E. D'Anna, A. D'Innocenzo, G. Leggieri, A. Perrone and G. Discherl, 1977, Chem. Phys. Lett. 47, 241.
- Cotton, F.A., and G. Wilkinson, 1988, Advanced Inorganic Chemistry, 5th Ed. (Wiley, New York) ch. 21.
- Cowan, R.D., and D.C. Griffin, 1976, J. Opt. Soc. Am. 66, 1010.
- Culberson, J.C., P. Knappe, N. Rösch and M.C. Zerner, 1987, Theor. Chim. Acta 71, 21.
- Cundari, T.R., 1992, J. Am. Chem. Soc. 114, 7879.
- Cundari, T.R., and W.J. Stevens, 1993, J. Chem. Phys. 98, 5555.
- Cundari, T.R., W.J. Stevens and S.O. Sommerer, 1993, Chem. Phys. 178, 235.
- Cundari, T.R., S.O. Sommerer, L.A. Strohdecker and L. Tippett, 1995, J. Chem. Phys. 103, 7058.
- Das, K.K., and K. Balasubramanian, 1990, Chem. Phys. Lett. 172, 372.
- Das, K.K., and K. Balasubramanian, 1991a, J. Phys. Chem. 95, 42.
- Das, K.K., and K. Balasubramanian, 1991b, J. Chem. Phys. 94, 3722.
- Datta, S.N., C.S. Ewig and J.R. van Wazer, 1978, Chem. Phys. Lett. 57, 83.
- David, F., K. Samhoun, R. Guillaumont and N.M. Edelstein, 1978, J. Inorg. Nucl. Chem. 40, 69.
- DeJong, W.A., L. Visscher, O. Visser, P.J.C. Aerts and W.C. Nieuwpoort, 1994, MOLFDIR: a program package for molecular Dirac-Fock-CI calculations, in: New Challenges in Computational Quantum Chemistry, eds R. Broer, P.J.C. Aerts and P.S. Bagus (Department of Chemical Sciences and Material Science Centre, University of Groningen, Netherlands).
- DeKock, C.W., R.D. Wesley and D.D. Radtke, 1972, High Temp. Sci. 4, 41.
- DeKock, L., and W. Weltner, 1971, J. Phys. Chem. 75, 514.

- DeKock, R.L., M.A. Peterson, L.K. Timmer, E.J. Baerends and P. Vernooijs, 1990, Polyhedron 9, 1919; erratum: 1991, Polyhedron 10, 1965.
- Desclaux, J.P., 1972, Int. J. Quantum Chem. 6, 25.
- Desclaux, J.P., 1973, At. Data Nucl. Data Tab. 12, 311.
- Desclaux, J.P., 1975, Comput. Phys. Commun. 9, 31.
- Desclaux, J.P., 1977, Comput. Phys. Commun. 13, 71.
- Desclaux, J.P., 1983a, Numerical Dirac–Fock calculations for atoms, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 115.
- Desclaux, J.P., 1983b, Dirac–Fock one-centre expansion method, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 213.
- Desclaux, J.P., and B. Fricke, 1980, J. Phys. (France) 41, 943.
- Desclaux, J.P., and P. Pyykkö, 1974, Chem. Phys. Lett. **29**, 534.
- Desclaux, J.P., and P. Pyykkö, 1976, Chem. Phys. Lett. **39**, 300.
- Dewar, M.J.S., and W.J. Thiel, 1977a, J. Am. Chem. Soc. 99, 4899.
- Dewar, M.J.S., and W.J. Thiel, 1977b, J. Am. Chem. Soc. 99, 4907.
- Dewar, M.J.S., E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, 1985, J. Am. Chem. Soc. 107, 3902.
- DiBella, S., G. Lanza and I.L. Fragalà, 1993, Chem. Phys. Lett. 214, 598.
- Dirac, P.A.M., 1928a, Proc. R. Soc. A 117, 610.
- Dirac, P.A.M., 1928b, Proc. R. Soc. A 118, 351.
- Dirac, P.A.M., 1929, Proc. R. Soc. A 123, 714.
- Dixon, R.N., and I.L. Robertson, 1978, The use of pseudopotentials in molecular calculations, in: Specialist Periodical Reports, Theoretical Chemistry, Vol. 3, ed. R.N. Dixon (Chemical Society, London) p. 100.
- Dolg, M., 1989, Energiejustierte quasirelativistische Pseudopotentiale f
 ür die 4f-Elemente, Doktorarbeit (Universit
 ät Stuttgart).
- Dolg, M., 1995, unpublished results.
- Dolg, M., and H. Stoll, 1989, Theor. Chim. Acta 75, 369.
- Dolg, M., U. Wedig, H. Stoll and H. Preuß, 1987, J. Chem. Phys. 86, 866.
- Dolg, M., H. Stoll and H. Preuß, 1989a, J. Chem. Phys. 90, 1730.

- Dolg, M., H. Stoll, A. Savin and H. Preuß, 1989b, Theor. Chim. Acta **75**, 173.
- Dolg, M., H. Stoll, A. Savin and H. Preuß, 1989c, Pseudopotential study of rare earth compounds, in: Quantum Chemistry – Basic Aspects, Actual Trends, Studies in Physical and Theoretical Chemistry, Vol. 62, ed. R. Carbó (Elsevier, Amsterdam) p. 265.
- Dolg, M., H. Stoll and H. Preuß, 1990a, Chem. Phys. Lett. 174, 208.
- Dolg, M., H. Stoll and H. Preuß, 1990b, Chem. Phys. 148, 219.
- Dolg, M., H. Stoll and H. Preuß, 1991a, J. Mol. Struct. (Theochem) 231, 243.
- Dolg, M., H. Stoll and H. Preuß, 1991b, J. Mol. Struct. (Theochem) 235, 67.
- Dolg, M., H. Stoll and H. Preuß, 1991c, J. Mol. Struct. (Theochem) **251**, 327.
- Dolg, M., P. Fulde, W. Küchle, C.-S. Neumann and H. Stoll, 1991d, J. Chem. Phys. 94, 3011.
- Dolg, M., H. Stoll and H. Preuß, 1992a, J. Mol. Struct. (Theochem) **277**, 239.
- Dolg, M., H. Stoll and H. Preuß, 1992b, Chem. Phys. 165, 21.
- Dolg, M., H. Stoll, H.-J. Flad and H. Preuß, 1992c, J. Chem. Phys. 97, 1162.
- Dolg, M., H. Stoll and H. Preuß, 1993a, Theor. Chim. Acta 85, 441.
- Dolg, M., H. Stoll, H. Preuß and R.M. Pitzer, 1993b, J. Phys. Chem. 97, 5852.
- Dolg, M., P. Fulde, H. Stoll, H. Preuß, A.H.H. Chang and R.M. Pitzer, 1995, Chem. Phys. 195, 71.
- Dong, N., L. Zhu and N. Wu, 1992, Chin. Chem. Lett. 3, 649. (CA 118: 109931k.).
- Douglas, M., and N.M. Kroll, 1974, Ann. Phys. 82, 89.
- Dulick, M., 1982, Spectroscopic studies of the diatomic rare-earth oxides, Thesis (MIT, Cambridge, MA).
- Dulick, M., and R.W. Field, 1985, J. Mol. Spectrosc. 113, 105.
- Dulick, M., R.W. Field, J.C. Beaufils and J. Schamps, 1981, J. Mol. Spectrosc. 87, 278.
- Dulick, M., E. Murad and R.F. Barrow, 1986, J. Chem. Phys. 85, 385.
- Dunlap, B.I., and N. Rösch, 1990, Adv. Quantum Chem. 21, 317.
- Durand, P., and J.C. Barthelat, 1974, Chem. Phys. Lett. **27**, 191.
- Durand, P., and J.C. Barthelat, 1975, Theor. Chim. Acta 38, 283.

- Dyall, K.G., 1994a, Polyatomic molecular Dirac– Hartree–Fock calculations with Gaussian basis sets: theory, implementation and applications, in: Relativistic and Electron Correlation Effects in Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 318, ed. G.L. Malli (Plenum, New York) p. 17.
- Dyall, K.G., 1994b, J. Chem. Phys. 100, 2118.
- Dyall, K.G., 1994c, Chem. Phys. Lett. 224, 186.
- Dyall, K.G., I.P. Grant, C.T. Johnson, F.A. Parpia and E.P. Plummer, 1989, Comput. Phys. Commun. 55, 425.
- Dyall, K.G., P.R. Taylor, K. Faegri and H. Partridge, 1991, J. Chem. Phys. 95, 2583.
- Einstein, A., 1905, Ann. Phys. 27, 891.
- Eliav, E., U. Kaldor and Y. Ishikawa, 1994a, Phys. Rev. A 49, 1724.
- Eliav, E., U. Kaldor, P. Schwerdtfeger, B.A. Hess and Y. Ishikawa, 1994b, Phys. Rev. Lett. **73**, 3203.
- Eliav, E., U. Kaldor and Y. Ishikawa, 1995, Phys. Rev. A 51, 225.
- Ellis, D.E., and G.L. Goodman, 1984, Int. J. Quantum Chem. 25, 185.
- Ermler, W.C., R.B. Ross and P.A. Christiansen, 1988, Adv. Quantum Chem. 19, 139.
- Ermler, W.C., R.B. Ross and P.A. Christiansen, 1991, Int. J. Quantum Chem. 40, 829.
- Esser, M., 1983, Entwicklung einer relativistischen direkten MRCI-Methode zur Berechnung von schweratomigen Systemen, Doktorarbeit (Universität Siegen).
- Esser, M., 1984a, Int. J. Quantum Chem. 26, 313.
- Esser, M., 1984b, Chem. Phys. Lett. 111, 58.
- Esser, M., W. Butscher and W.H.E. Schwarz, 1981, Chem. Phys. Lett. 77, 359.
- Fanning, M.O., and N.J. Fitzpatrick, 1980, Int. J. Quantum Chem. 28, 1339.
- Fényes, I., 1943, Csillagászati Lapok (Budapest) 6, 49.
- Field, R.W., 1982, Ber. Bunsenges. Phys. Chem. 86, 771.
- Fleig, T., and C.M. Marian, 1994, Chem. Phys. Lett. 222, 267.
- Fock, V., 1930, Z. Phys. 61, 126.
- Foldy, L.L., and S.A. Wouthuysen, 1950, Phys. Rev. 78, 29.
- Frenking, G., and D. Cremer, 1990, Structure and Bonding, Vol. 73 (Springer, Berlin) p. 17.
- Froese Fischer, C., 1977, The Hartree–Fock Method for Atoms – A Numerical Approach (Wiley, New York).

- Froese Fischer, C., 1991a, Comput. Phys. Commun. 64, 369.
- Froese Fischer, C., 1991b, Comput. Phys. Commun. 64, 431.
- Froese Fischer, C., 1991c, Comput. Phys. Commun. 64, 473.
- Froese Fischer, C., and M.R. Godefroid, 1991, Comput. Phys. Commun. 64, 501.
- Froese Fischer, C., and B. Liu, 1991, Comput. Phys. Commun. 64, 406.
- Fuentealba, P., H. Preuß, H. Stoll and L. v. Szentpály, 1982, Chem. Phys. Lett. 89, 418.
- Fuentealba, P., L. v. Szentpály, H. Preuß and H. Stoll, 1985, J. Phys. B 18, 1287.
- Fuentealba, P., O. Reyes, H. Stoll and H. Preuß, 1987, J. Chem. Phys. 87, 5338.
- Fulde, P., 1991, Electron Correlations in Molecules and Solids, Solid-State Sciences, Vol. 100 (Springer, Berlin).
- Gabelnick, S.D., G.T. Reedy and M.G. Chasanov, 1974, J. Chem. Phys. 60, 1167.
- Gaunt, J.A., 1929a, Proc. R. Soc. A 122, 513.
- Gaunt, J.A., 1929b, Proc. R. Soc. A 124, 163.
- Gérard, I., H. Chermette and J.C. Krupa, 1994, in: REMCES VI, Adv. Mater. Res. Proc. 1, 89.
- Gleichmann, M.M., and B.A. Hess, 1994, Chem. Phys. Lett. 227, 299.
- Gombás, P., 1935, Z. Phys. 94, 473.
- Gordon, W., 1926, Z. Phys. 40, 117.
- Gotkis, I., 1991, J. Phys. Chem. 95, 6086.
- Grant, I.P., 1961, Proc. R. Soc. A 262, 555.
- Grant, I.P., 1970, Adv. Phys. 19, 747.
- Grant, I.P., 1983a, Incidence of relativistic effects in atoms, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 55.
- Grant, I.P., 1983b, Formulation of the relativistic *N*electron problem, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 73.
- Grant, I.P., 1983c, Techniques for open shell calculations for atoms, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 89.
- Grant, I.P., 1983d, Self-consistency and numerical problems, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 101.

Grant, I.P., 1984, Int. J. Quantum Chem. 25, 23.

- Grant, I.P., 1986, Aust. J. Phys. 39, 649.
- Grant, I.P., 1988, Relativistic atomic structure calculations, in: Relativistic Effects in Atoms and Molecules, Methods in Computational Chemistry, Vol. 2, ed. S. Wilson (Plenum, New York).
- Grant, I.P., and H.M. Quiney, 1988, Adv. At. Mol. Phys. 23, 37.
- Grant, I.P., B.J. McKenzie, P.H. Norrington, D.F. Mayers and N.C. Pyper, 1980, Comput. Phys. Commun. 21, 207.
- Greco, A., S. Cesca and G. Bertolini, 1976, J. Organometal. Chem. 113, 321.
- Gropen, O., 1988, The relativistic effective core potential method, in: Relativistic Effects in Atoms and Molecules, Methods in Computational Chemistry, Vol. 2, ed. S. Wilson (Plenum, New York).
- Guido, M., and G. Gigli, 1974, J. Chem. Phys. 61, 4138.
- Guo, C., and D.E. Ellis, 1984, J. Lumin. 31-32, 210.
- Guo, T., M.D. Diener, Y. Chai, M.J. Alford, R.E. Haufler, S.M. McClure, T. Ohno, J.H. Weaver, G.E. Scuseria and R.E. Smalley, 1992, Science 257, 1661.
- Häberlen, O.D., and N. Rösch, 1992, Chem. Phys. Lett. 199, 491.
- Häberlen, O.D., N. Rösch and B.I. Dunlap, 1992, Chem. Phys. Lett. 200, 418.
- Hafner, P., and W.H.E. Schwarz, 1979, Chem. Phys. Lett. 65, 537.
- Hafner, P., P. Habitz, Y. Ishikawa, E. Wechsel-Trakowski and W.H.E. Schwarz, 1981, Chem. Phys. Lett. **80**, 311.
- Haghighi, M.S., C.L. Teske and H. Homborg, 1992, Z. Anorg, Allg. Chem. 608, 73.
- Hamann, D.R., M. Schlüter and C. Chiang, 1979, Phys. Rev. Lett. 43, 1491.
- Hariharan, A.V., and H.A. Eick, 1972a, High Temp. Sci. 4, 91.
- Hariharan, A.V., and H.A. Eick, 1972b, High Temp. Sci. 4, 379.
- Hariharan, A.V., N.A. Fishel and H.A. Eick, 1972, High Temp. Sci. 4, 405.
- Hartree, D.R., 1928a, Proc. Cambridge Philos. Soc. 24, 89.
- Hartree, D.R., 1928b, Proc. Cambridge Philos. Soc. 24, 111.
- Hartree, D.R., 1929, Proc. Cambridge Philos. Soc. 25, 225.

- Hartree, D.R., 1957, The Calculation of Atomic Structures (Chapman and Hall, London).
- Hastie, J.W., R.H. Hauge and J.L. Margrave, 1971, High Temp. Sci. 3, 56.
- Hay, P.J., 1983, Electronic structure of molecules using relativistic effective core potentials, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 383.
- Hay, P.J., and W.R. Wadt, 1985a, J. Chem. Phys. 82, 270.
- Hay, P.J., and W.R. Wadt, 1985b, J. Chem. Phys. 82, 299.
- Hayes, E.F., 1966, J. Chem. Phys. 70, 3740.
- Hazi, A.U., and S.A. Rice, 1968, J. Chem. Phys. 48, 495.
- Heinemann, C., H.H. Cornehl, D. Schröder, M. Dolg and H. Schwarz, 1996, Inorg. Chem., in press.
- Heisenberg, W., 1925, Z. Phys. 33, 879.
- Hellmann, H., 1935, J. Chem. Phys. 3, 61.
- Hess, B.A., 1986, Phys. Rev. A 33, 3742.
- Heully, J.-L., I. Lindgren, E. Lindroth, S. Lundqvist and A.-M. Mårtensson-Pendrill, 1986, J. Phys. B 19, 2799.
- Hibbert, A., and C. Froese Fischer, 1991, Comput. Phys. Commun. 64, 417.
- Hibbert, A., R. Glass and C. Froese Fischer, 1991, Comput. Phys. Commun. 64, 455.
- Hodgson, K.O., F. Mares, D.F. Starks and A. Streitwieser, 1973, J. Am. Chem. Soc. 95, 8650.
- Hoffmann, R., 1963, J. Chem. Phys. 39, 1397.
- Hoffmann, R., and W.N. Lipscomb, 1962a, J. Chem. Phys. 36, 2179.
- Hoffmann, R., and W.N. Lipscomb, 1962b, J. Chem. Phys. 37, 2871.
- Hohenberg, P., and W. Kohn, 1964, Phys. Rev. B 136, 864.
- Hosoya, H., S. Yamabe, K. Morokuma and K. Ohno, 1993, Quantum Chemistry Literature Data Base (1978–1992), Release 1993 (The Institute for Molecular Science and National Center for Science Information System, Tokyo).
- Hotokka, M., T. Kindstedt, P. Pyykkö and B.O. Roos, 1984, Mol. Phys. 52, 23.
- Hu, C.D., and D.C. Langreth, 1985, Phys. Scripta 32, 391.
- Huang, L., C. Huang, J. Ren, G. Xu and C. He, 1991, Gaodeng Xuexiao Huaxue Xuebao 12, 290. (CA 115: 293506n.).

- Huber, K.P., and G. Herzberg, 1979, Molecular Spectra and Molecular Structure, Vol. IV, Constants of Diatomic Molecules (Van Nostrand, New York).
- Hurley, M.M., L.F. Pacios, P.A. Christiansen, R.B. Ross and W.C. Ermler, 1986, J. Chem. Phys. 84, 6840.
- Huron, B., J.P. Malrieu and P. Rancurel, 1973, J. Chem. Phys. 58, 5745.
- Huzinaga, S., L. Seijo, Z. Barandiarán and M. Klobukowski, 1987, J. Chem. Phys. 86, 2132.
- Igel-Mann, G., H. Stoll and H. Preuß, 1988, Mol. Phys. 65, 1321.
- Isago, H., and M. Shimoda, 1992, Chem. Lett. 150, 147.
- Ishikawa, Y., 1990, Int. J. Quantum Chem. Symp. 24, 383.
- Ishikawa, Y., and G.L. Malli, 1981, J. Chem. Phys. 75, 5423.
- Ishikawa, Y., and G.L. Malli, 1983, Fully relativistic effective core potentials, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 363.
- Itoh, T., 1965, Rev. Mod. Phys. 37, 157.
- Itzykson, C., and J.-B. Zuber, 1980, Quantum Field Theory (McGraw-Hill, New York).
- Jahns, V., S. Köstlmeier, M. Kotzian, N. Rösch and P.L. Watson, 1992, Int. J. Quantum Chem. 44, 853.
- Jankowski, K., and A. Rutkowski, 1987, Physica Scripta 36, 464.
- Jansen, G., and B.A. Hess, 1989a, Phys. Rev. A 39, 6016.
- Jansen, G., and B.A. Hess, 1989b, Chem. Phys. Lett. 160, 507.
- Jia, Y.Q., 1987, Inorg. Chim. Acta, 132, 289.
- Jia, Y.Q., and S.G. Zhang, 1988, Inorg. Chim. Acta 143, 137.
- Johnson, R.D., M.S. de Vries, J. Salem, D.S. Bethune and C.S. Yannoni, 1992, Nature 355, 239.
- Jørgensen, C.K., 1988, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 11, eds K.A. Gschneidner Jr and L. Eyring (Elsevier, Amsterdam) p. 197.
- Jørgensen, C.K., 1989, in: Topics in Current Chemistry, Vol. 150 (Springer, Berlin).
- Jørgensen, C.K., and G. Frenking, 1990, Structure and Bonding, Vol. 73 (Springer, Berlin) p. 1.
- Jørgensen, C.K., R. Pappalardo and H.-H. Schmidtke, 1963, J. Chem. Phys. 39, 1422.
- Kagawa, T., 1975, Phys. Rev. A 12, 2245.
- Kahn, L.R., 1984, Int. J. Quantum Chem. 25, 149.

- Kahn, L.R., P. Baybutt and D. Truhlar, 1976, J. Chem. Phys. 65, 3826.
- Kahn, L.R., P.J. Hay and R.D. Cowan, 1978, J. Chem. Phys. 68, 2386.
- Kaldor, U., and B.A. Hess, 1994, Chem. Phys. Lett. 230, 1.
- Kaledin, L.A., J.E. McCord and M.C. Heaven, 1993, J. Mol. Spectrosc. 158, 40.
- Kaledin, L.A., M.G. Erickson and M.C. Heaven, 1994, J. Mol. Spectrosc. 165, 323.
- Karwowski, J., and J. Kobus, 1985, Int. J. Quantum Chem. 28, 741.
- Kaufman, J.J., and L.M. Sachs, 1969, J. Chem. Phys. 51, 2992.
- Kaupp, M., and P.v.R. Schleyer, 1992, J. Phys. Chem. 96, 7316.
- Kaupp, M., O.P. Charkin and P.v.R. Schleyer, 1992, Organometallics 11, 2765.
- Kaupp, M., P.v.R. Schleyer, M. Dolg and H. Stoll, 1993, J. Am. Chem. Soc. 114, 8202.
- Kim, Y.K., 1967, Phys. Rev. 154, 17.
- Kirkwood, A.D., K.D. Bier, J.K. Thompson, T.L. Haslett, A.S. Huber and M. Moskovits, 1991, J. Phys. Chem. 95, 2644.
- Klein, O., 1927, Z. Phys. 41, 407.
- Kleinman, L., 1980, Phys. Rev. B 21, 2630.
- Klobukowski, M., 1983, J. Comp. Chem. 4, 350.
- Knappe, P., and N. Rösch, 1990, J. Chem. Phys. 92, 1153.
- Kobayashi, H., K. Okada, Y. Kaizu, N. Hamada and H. Adachi, 1987, Mol. Phys. 60, 561.
- Kobayashi, K., S. Nagase and T. Akasaka, 1995, Chem. Phys. Lett. 245, 230.
- Kobus, J., 1986, Acta Phys. Polon. B 17, 771.
- Kobus, J., and W. Jaskólski, 1987, J. Phys. B 20, 4949.
- Koch, W., J.R. Collins and G. Frenking, 1986, Chem. Phys. Lett. 132, 330.
- Koch, W., G. Frenking, J. Gauss, D. Cremer and J.R. Collins, 1987, J. Am. Chem. Soc. 109, 5917.
- Koelling, D.D., and A.H. MacDonald, 1983, Relativistic effects in solids, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 227.
- Kohn, W., and L.J. Sham, 1965, Phys. Rev. A 140, 1133.
- Kotzian, M., 1991, Spin–Bahn-Wechselwirkung im INDO/S-CI-Verfahren: Methodische Entwicklung, Parametrisierung der Lanthanoidenelemente und

Anwendungen, Doktorarbeit (Technische Universität München).

- Kotzian, M., and N. Rösch, 1991a, J. Mol. Spectrosc. 147, 346.
- Kotzian, M., and N. Rösch, 1991b, Eur. J. Solid State Inorg. Chem. 28, 127.
- Kotzian, M., and N. Rösch, 1992, J. Phys. Chem. 96, 7288.
- Kotzian, M., N. Rösch, R.M. Pitzer and M.C. Zerner, 1989a, Chem. Phys. Lett. 160, 168.
- Kotzian, M., N. Rösch and M.C. Zerner, 1991, Int. J. Quantum Chem. Symp. 25, 545.
- Kotzian, M., N. Rösch and M.C. Zerner, 1992, Theor. Chim. Acta 81, 201.
- Kotzian, M., T. Fox and N. Rösch, 1995, J. Phys. Chem. 99, 600.
- Krasnov, K.S., N.I. Giricheva and G.V. Girichev, 1976, Zh. Strukt. Khim. 17, 677.
- Krasnov, K.S., G.V. Girichev, N.I. Giricheva, V.M. Petrov, E.Z. Zasorin and N.I. Popenko, 1978, in: 7th Austin Symp. on Gas-phase Molecular Structure (Austin, TX) p. 88.
- Krauss, M., and W.J. Stevens, 1984, Annu. Rev. Phys. Chem. 35, 357.
- Kroto, H.W., J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, 1985, Nature 318, 162.
- Küchle, W., 1993, Pseudopotentiale für Aktinoide, Diplomarbeit (Universität Stuttgart).
- Küchle, W., M. Dolg, H. Stoll and H. Preuß, 1991, Mol. Phys. 74, 1245.
- Küchle, W., M. Dolg, H. Stoll and H. Preuß, 1994, J. Chem. Phys. 100, 7535.
- Küchle, W., M. Dolg, H. Stoll and R.M. Pitzer, 1995, unpublished results.
- Kulikov, A.N., L.A. Kaledin, A.I. Kobyliansky and L.V. Gurvich, 1984, Can. J. Phys. 62, 1855.
- Kutzelnigg, W., 1984, Int. J. Quantum Chem. 25, 107.
- Kutzelnigg, W., 1987, Phys. Scripta 36, 416.
- Kutzelnigg, W., 1990, Z. Phys. D 15, 27.
- Kutzelnigg, W., E. Ottschofski and R. Franke, 1995, J. Chem. Phys. 102, 1740.
- Laasonen, K., W. Andreoni and M. Parrinello, 1992, Science 258, 1916.
- LaJohn, L.A., P.A. Christiansen, R.B. Ross, T. Atashroo and W.C. Ermler, 1987, J. Chem. Phys. 87, 2812.
- Lan, G., and Z. Li, 1992, Zhongguo Xitu Xuebao 10, 9. (CA 120: 38565x.).
- Langhoff, S.R., and E.R. Davidson, 1974, Int. J. Quantum Chem. 8, 61.

- Larsson, S., and P. Pyykkö, 1986, Chem. Phys. 101, 355.
- Lee, S.Y., and Y.S. Lee, 1992, J. Comput. Chem. 13, 595.
- Lee, Y.S., W.C. Ermler and K.S. Pitzer, 1977, J. Chem. Phys. 67, 5861.
- Li, J., J. Ren, G. Xu and C. Qian, 1986b, Inorg. Chim. Acta 122, 255.
- Li, J., J. Ren and G. Xu, 1987a, Inorg. Chem. 26, 1077.
- Li, L., J. Ren, G. Xu and X. Wang, 1983, Int. J. Quantum Chem. 23, 1305.
- Li, Z., J. Ni, G. Xu and L. Li, 1986a, Wuji Huaxue 2, 8. (CA 106: 202111e.).
- Li, Z., S. Wang and F. Wang, 1986c, Yingyong Huaxue 3, 72. (CA 106: 90390m.).
- Li, Z., W. Chen, G. Xu and J. Ren, 1987b, Wuji Huaxue 3, 111. (CA 109: 129194q.).
- Lindgren, I., and A. Rosén, 1974, Case Stud. At. Phys. 4, 93.
- Linton, C., S. McDonald, S. Rice, M. Dulick, Y.C. Liu and R.W. Field, 1983a, J. Mol. Spectrosc. 101, 332.
- Linton, C., M. Dulick, R.W. Field, P. Carette, P.C. Leyland and R.F. Barrow, 1983b, J. Mol. Spectrosc. 102, 441.
- Lohr, L.L., 1987, Inorg. Chem. 26, 2005.
- Lohr, L.L., and Y.Q. Jia, 1986, Inorg. Chim. Acta 119, 99.
- Lohr, L.L., and W.N. Lipscomb, 1963, J. Chem. Phys. 38, 1607.
- Lohr, L.L., and P. Pyykkö, 1979, Chem. Phys. Lett. 62, 333.
- Mackrodt, W.C., 1970, Mol. Phys. 18, 697.
- Malli, G.L., 1980, Chem. Phys. Lett. 73, 510.
- Malli, G.L., ed., 1983a, Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87 (Plenum, New York).
- Malli, G.L., 1983b, Relativistic self-consistent field theory for molecules, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 183.
- Malli, G.L., 1988, Ab-initio relativistic quantum chemistry, in: Molecules in Physics, Chemistry and Biology, Vol. 2, ed. J. Maruani (Kluwer, Dordrecht) p. 85.
- Malli, G.L., ed., 1994a, Relativistic and Electron Correlation Effects in Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 318 (Plenum, New York).

- Malli, G.L., 1994b, Relativistic and electron correlation effects in molecules of heavy elements, in: Relativistic and Electron Correlation Effects in Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 318, ed. G.L. Malli (Plenum, New York) p. 1.
- Malli, G.L., and J. Oreg, 1975, J. Chem. Phys. 63, 830.
- Malli, G.L., and N.C. Pyper, 1986, Proc. R. Soc. A 407, 377.
- Mann, J.B., and W.R. Johnson, 1971, Phys. Rev. A 4, 41.
- Mann, J.B., and J.T. Waber, 1973, Atomic Data 5, 102.
- Marian, C.M., U. Wahlgren, O. Gropen and P. Pyykkö, 1988, J. Molec. Struct. (Theochem) 46, 339.
- Mark, F., and F. Rosicky, 1980, Chem. Phys. Lett. 74, 562.
- Mark, F., and W.H.E. Schwarz, 1982, Phys. Rev. Lett. 48, 673.
- Mark, F., H. Lischka and F. Rosicky, 1980, Chem. Phys. Lett. 71, 507.
- Marks, T.J., 1978, Prog. Inorg. Chem. 24, 51.
- Marks, T.J., and R.D. Ernst, 1982, in: Comprehensive Organometallic Chemistry, Vol. 3, eds G. Wilkinson, F.G.A. Stone and E.W. Abel (Pergamon, New York) p. 173.
- Marks, T.J., and R.D. Fischer, eds, 1979, Organometallics of the f-Elements (Reidel, Dordrecht).
- Márquez, A., M.J. Capitán, J.A. Odriozola and J.F. Sanz, 1994, Int. J. Quantum Chem. 52, 1329.
- Martin, R.L., 1983, J. Phys. Chem. 87, 750.
- Martin, R.L., and P.J. Hay, 1981, J. Chem. Phys. 75, 4539.
- Martin, W.C., R. Zalubas and L. Hagan, 1978, Atomic Energy Levels – The Rare Earth Elements, NSRDS-NBS-60 (National Bureau of Standards, US Dept. of Commerce, Washington, DC).
- Matsuoka, O., N. Suzuki, T. Ayoma and G.L. Malli, 1980, J. Chem. Phys. 73, 1320.
- McDonald, S.A., 1985, Spectroscopy of diatomic rare-earth oxides: YbO and EuO, Thesis (MIT, Cambridge, MA).
- McDonald, S.A., S.F. Rice, R.W. Field and C. Linton, 1990, J. Chem. Phys. **93**, 7676.
- Min, X., 1992a, Huaxue Xuebao 50, 449. (CA 117: 111728x.).
- Min, X., 1992b, Huaxue Xuebao 50, 1098. (CA 119: 8916z.).
- Mohanty, A.K., and E. Clementi, 1991, Int. J. Quantum Chem. **39**, 487.

- Moore, C.E., 1949, Atomic Energy Levels, Circular 467 (National Bureau of Standards, US Dept. of Commerce, Washington, DC) Vol. I.
- Moore, C.E., 1952, Atomic Energy Levels, Circular 467 (National Bureau of Standards, US Dept. of Commerce, Washington, DC) Vol. II.
- Moore, C.E., 1958, Atomic Energy Levels, Circular 467 (National Burcau of Standards, US Dept. of Commerce, Washington, DC) Vol. III.
- Murad, E., and D.L. Hildenbrand, 1980, J. Chem. Phys. **73**, 4005.
- Myers, C.E., 1975, Inorg. Chem. 14, 199.
- Myers, C.E., 1976, Inorg. Nucl. Chem. Lett. 12, 575.
- Myers, C.E., and D.T. Graves, 1977, J. Chem. Eng. Data 22, 436.
- Myers, C.E., L.J. Norman and L.M. Loew, 1978, Inorg. Chem. 17, 1581.
- Nagase, S., and K. Kobayashi, 1993, Chem. Phys. Lett. 214, 57.
- Nagase, S., and K. Kobayashi, 1994, Chem. Phys. Lett. 228, 106.
- Nagase, S., K. Kobayashi, T. Kato and Y. Achiba, 1993, Chem. Phys. Lett. 201, 475.
- Neumann, C.-S., and P. Fulde, 1989, Z. Phys. B 74, 277.
- Nieuwpoort, W.C., P.J.C. Aerts and L. Visscher, 1994, Molecular electronic structure calculations based on the Dirac–Coulomb–(Breit) Hamiltonian, in: Relativistic and Electron Correlation Effects in Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 318, ed. G.L. Malli (Plenum, New York) p. 59.
- Ohta, K., Y. Yoshioka, K. Morokuma and K. Kitaura, 1983, Chem. Phys. Lett. 101, 12.
- Ortiz, J.V., and R. Hoffmann, 1985, Inorg. Chem. 24, 2095.
- Ottschofski, E., and W. Kutzelnigg, 1995, J. Chem. Phys. 102, 1752.
- Pacios, L.F., and P.A. Christiansen, 1985, J. Chem. Phys. 82, 2664.
- Park, C., and J. Almloef, 1991, J. Chem. Phys. 95, 1829.
- Pepper, M., and B.E. Bursten, 1991, Chem. Rev. 91, 719.
- Perdew, J.P., 1986, Phys. Rev. B 33, 8822.
- Petzel, T., and O. Greis, 1972, Z. Anorg. All. Chem. 338, 137.
- Phillips, J.C., and L. Kleinman, 1959, Phys. Rev. 116, 287.
- Pitzer, K.S., 1979, Acc. Chem. Res. 12, 271.

- Pitzer, K.S., 1983, Electron structure of molecules with very heavy atoms using effective core potentials, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 403.
- Pitzer, K.S., 1984, Int. J. Quantum Chem. 25, 131.
- Pitzer, R.M., and N.W. Winter, 1988, J. Phys. Chem. 92, 3061.
- Popenko, N.I., E.Z. Zasorin, V.P. Spiridonov and A.A. Ivanov, 1978, Inorg. Chim. Acta 31, L371.
- Pople, J.A., and D.L. Beveridge, 1970, Approximate Molecular Orbital Theory (McGraw-Hill, New York).
- Pople, J.A., D.P. Santry and G.A. Segal, 1965, J. Chem. Phys. 43, S129.
- Pople, J.A., D.L. Beveridge and P.A. Dobosh, 1967, J. Chem. Phys. 47, 158.
- Preuß, H., 1955, Z. Naturf. 10a, 365.
- Pyper, N.C., 1980a, Mol. Phys. 39, 1327.
- Pyper, N.C., 1980b, Mol. Phys. 41, 949.
- Pyper, N.C., 1981, Mol. Phys. 42, 1059.
- Pyper, N.C., and P. Marketos, 1981, Mol. Phys. 42, 1073.
- Pyykkö, P., 1978, Adv. Quantum Chem. 11, 353.
- Pyykkö, P., 1979a, J. Chem. Soc., Faraday Trans. 2, 75, 1256.
- Pyykkö, P., 1979b, Phys. Scripta 20, 647.
- Pyykkö, P., 1979c, J. Chem. Research (S), 380.
- Pyykkö, P., ed., 1984, Int. J. Quantum Chem. 25, 1– 256.
- Pyykkö, P., 1986, Relativistic Theory of Atoms and Molecules. A Bibliography 1916–1985, Lecture Notes in Chemistry, Vol. 41 (Springer, Berlin).
- Pyykkö, P., 1987, Inorg. Chim. Acta 139, 243.
- Pyykkö, P., 1988a, Chem. Rev. 88, 563.
- Pyykkö, P., 1988b, Semiempirical relativistic molecular structure calculations, in: Relativistic Effects in Atoms and Molecules, Methods in Computational Chemistry, Vol. 2, ed. S. Wilson (Plenum, New York).
- Pyykkö, P., 1993, Relativistic Theory of Atoms and Molecules II. A Bibliography 1986–1992, Lecture Notes in Chemistry, Vol. 60 (Springer, Berlin).
- Pyykkö, P., and J.P. Desclaux, 1977, Chem. Phys. Lett. 50, 503.
- Pyykkö, P., and J.P. Desclaux, 1978, Chem. Phys. 34, 261.
- Pyykkö, P., and J.P. Desclaux, 1979a, Acc. Chem. Res. 12, 276.

- Pyykkö, P., and J.P. Desclaux, 1979b, J. Phys. Colloq. C4, 222.
- Pyykkö, P., and L.L. Lohr, 1981, Inorg. Chem. 20, 1950.
- Pyykkö, P., J.G. Snijders and E.J. Baerends, 1981, Chem. Phys. Lett. 83, 432.
- Pyykkö, P., L.J. Laakkonen and K. Tatsumi, 1989, Inorg. Chem. 28, 1801.
- Quiney, H.M., 1988, Relativistic many-body perturbation theory, in: Relativistic Effects in Atoms and Molecules, Methods in Computational Chemistry, Vol. 2, ed. S. Wilson (Plenum, New York).
- Rabaâ, H., J.-Y. Saillard and R. Hoffmann, 1986, J. Am. Chem. Soc. 108, 4327.
- Racah, G., 1942a, Phys. Rev. 61, 186.
- Racah, G., 1942b, Phys. Rev. 62, 438.
- Racah, G., 1943, Phys. Rev. 63, 367.
- Racah, G., 1949, Phys. Rev. 76, 1352.
- Radzig, A.A., and B.M. Smirnov, 1985, Reference Data on Atoms, Molecules and Ions, Springer Series in Physics, Vol. 31 (Springer, Berlin).
- Ramana, M.V., and A.K. Rajagopal, 1983, Adv. Chem. Phys. 54, 231.
- Rappé, A.K., T. Smedley and W.A. Goddard III, 1981, J. Chem. Phys. 85, 2607.
- Ren, J., L. Li, X. Wang and G. Xu, 1982, Acta Sci. Natur. Univ. Pekinensis 3, 30.
- Ren, J., L. Li and G. Xu, 1983, Zhongguo Xitu Xuebao 1, 25. (CA 100: 215661k.).
- Rittner, E.S., 1951, J. Chem. Phys. 19, 1030.
- Roothaan, C.C.J., 1951, Rev. Mod. Phys. 23, 69.
- Roothaan, C.C.J., 1960, Rev. Mod. Phys. 32, 179.
- Rösch, N., 1983, Chem. Phys. 80, 1.
- Rösch, N., 1984, Inorg. Chim. Acta 94, 297.
- Rösch, N., and O.D. Häberlen, 1992, J. Chem. Phys. 96, 6322.
- Rösch, N., and A. Streitwieser, 1978, J. Organomet. Chem. 145, 195.
- Rösch, N., and A. Streitwieser, 1983, J. Am. Chem. Soc. 105, 7237.
- Rösch, N., O.D. Häberlen and B.I. Dunlap, 1993, Angew. Chem. 105, 78.
- Rose, S.J., I.P. Grant and N.C. Pyper, 1978, J. Phys. B 11, 1171.
- Rosén, A., and D.E. Ellis, 1975, J. Chem. Phys. 62, 3039.
- Rosén, A., and B. Wästberg, 1988, J. Am. Chem. Soc. 110, 8701.
- Rosén, A., and B. Wästberg, 1989, Z. Phys. D 12, 387.

- Rosén, A., D.E. Ellis, H. Adachi and F.W. Averill, 1976, J. Chem. Phys. 65, 3629.
- Rosicky, F., 1982, Chem. Phys. Lett. 85, 195.
- Ross, R.B., J.M. Powers, T. Atashroo, W.C. Ermler, L.A. LaJohn and P.A. Christiansen, 1990, J. Chem. Phys. 93, 6654.
- Ross, R.B., S. Gayen and W.C. Ermler, 1994, J. Chem. Phys. 100, 8145.
- Ruščić, B., G.L. Goodman and J. Berkowitz, 1983, J. Chem. Phys. 78, 5443.
- Rutkowski, A., 1986a, J. Phys. B 19, 149.
- Rutkowski, A., 1986b, J. Phys. B 19, 3431.
- Rutkowski, A., 1986c, J. Phys. B 19, 3443.
- Sakai, Y., and S. Huzinaga, 1982, J. Chem. Phys. 76, 2537.
- Sakai, Y., E. Miyoshi, M. Klobukowski and S. Huzinaga, 1987a, J. Comput. Chem. 8, 226.
- Sakai, Y., E. Miyoshi, M. Klobukowski and S. Huzinaga, 1987b, J. Comput. Chem. 8, 256.
- Salahub, D.R., and M.C. Zerner, eds, 1989, The Challenge of d and f Electrons, Theory and Computation, ACS Symposium Series, Vol. 394 (American Chemical Society, Washington, DC).
- Samzow, R., B.A. Hess and G. Jansen, 1992, J. Chem. Phys. 96, 1227.
- Schäffer, C.E., and C.K. Jørgensen, 1965, Mol. Phys. 9, 401.
- Schrödinger, E., 1926, Ann. Phys. 81, 109.
- Schwarz, W.H.E., 1968, Theor. Chim. Acta 11, 307.
- Schwarz, W.H.E., 1987, Phys. Scripta 36, 403.
- Schwarz, W.H.E., 1990, Fundamentals of relativistic effects in chemistry, in: Theoretical Models of Chemical Bonding, Part 2, The Concept of the Chemical Bond, ed. Z.B. Maksić (Springer, Berlin).
- Schwarz, W.H.E., and M. Kissel-Phillip, 1988, Phys. Rev. A 38, 6027.
- Schwarz, W.H.E., and H. Wallmeier, 1982, Mol. Phys. 46, 1045.
- Schwarz, W.H.E., and E. Wechsel-Trakowski, 1982, Chem. Phys. Lett. 85, 94.
- Schwarz, W.H.E., S.Y. Chu and F. Mark, 1983, Mol. Phys. 50, 603.
- Schwarz, W.H.E., E.M. van Wezenbeek, E.J. Baerends and J.G. Snijders, 1989, J. Phys. B 22, 1515.
- Schwerdtfeger, P., and M. Dolg, 1991, Phys. Rev. A 43, 1644.
- Seijo, L., Z. Barandiarán and S. Huzinaga, 1989, J. Chem. Phys. 91, 7011.
- Seth, M., M. Dolg, P. Fulde and P. Schwerdtfeger, 1995, J. Am. Chem. Soc. 117, 6597.

- Shannon, R.D., 1976, Acta Crystallogr. A 32, 751.
- Shannon, R.D., and C.T. Prewitt, 1969, Acta Crystallogr. B 25, 925.
- Slater, J.C., 1929, Phys. Rev. 35, 210.
- Snijders, J.G., and E.J. Baerends, 1978, Mol. Phys. 36, 1789.
- Snijders, J.G., and P. Pyykkö, 1980, Chem. Phys. Lett. 75, 5.
- Snijders, J.G., E.J. Baerends and P. Ros, 1979, Mol. Phys. 38, 1909.
- Sobelman, I.I., 1979, Atomic Spectra and Radiative Transitions, Springer Series in Chemical Physics, Vol. 1 (Springer, Berlin).
- Stanton, R.E., and S. Havriliak, 1984, J. Chem. Phys. 81, 1910.
- Stevens, W.J., and M. Krauss, 1982, Chem. Phys. Lett. 86, 320.
- Stevens, W.J., H. Basch and M. Krauss, 1984, J. Chem. Phys. 81, 6026.
- Stevens, W.J., M. Krauss, H. Basch and P.G. Jasien, 1992, Can. J. Chem. 70, 612.
- Stoll, H., C.M.E. Pavlidou and H. Preuß, 1978, Theor. Chim. Acta 49, 143.
- Stoll, H., E. Golka and H. Preuß, 1980, Theor. Chim. Acta 55, 29.
- Streitwieser, A., and U. Müller-Westerhoff, 1968, J. Am. Chem. Soc. 90, 7364.
- Streitwieser, A., and N. Yoshida, 1969, J. Am. Chem. Soc. 91, 7528.
- Streitwieser, A., S.A. Kinsley, J.T. Rigsbee, I.L. Fragalà, E. Ciliberto and N. Rösch, 1985, J. Am. Chem. Soc. 107, 7786.
- Strittmatter, R.J., and B.E. Bursten, 1991, J. Am. Chem. Soc. 113, 552.
- Sucher, J., 1983, Foundations of the relativistic theory of many-electron systems, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 1.
- Sucher, J., 1984, Int. J. Quantum Chem. 25, 3.
- Swirles, B., 1935, Proc. R. Soc. A 152, 625.
- Swirles, B., 1936, Proc. R. Soc. A 157, 680.
- Szasz, L., 1985, Pseudopotential Theory of Atoms and Molecules (Wiley, New York).
- Szépfalusy, P., 1955, Acta Phys. Acad. Sci. Hung. 5, 325.
- Szépfalusy, P., 1956, Acta Phys. Acad. Sci. Hung. 6, 273.
- Teichteil, C., M. Pélissier and F. Spiegelmann, 1983, Chem. Phys. 81, 273.

- Teichteil, C.H., J.P. Malrieu and J.C. Barthelat, 1977, Mol. Phys. 33, 181.
- Thornton, G., N. Rösch and N.M. Edelstein, 1980, Inorg. Chem. 19, 1304.
- Urland, W., 1976, Chem. Phys. 14, 393.
- Van Lenthe, E., E.J. Baerends and J.G. Snijders, 1993, J. Chem. Phys. 99, 4597.
- Van Lenthe, E., R. van Leeuwen, E.J. Baerends and J.G. Snijders, 1994, Relativistic regular twocomponent Hamiltonians, in: New Challenges in Computational Quantum Chemistry, eds R. Broer, P.J.C. Aerts and P.S. Bagus (Department of Chemical Sciences and Material Science Centre, University of Groningen, Netherlands).
- Van Piggelen, H.U., 1978, Ab initio calculations on the electronic states of $4f^{\pi}$ ions with applications to EuO_{6}^{2-} , Thesis (University of Groningen, Netherlands).
- Van Piggelen, H.U., 1980, J. Chem. Phys. 72, 3727.
- Van Zee, R.J., M.L. Seely and W. Weltner, 1977, J. Chem. Phys. 67, 861.
- Van Zee, R.J., M.L. Seely, T.C. De Vore and W. Weltner, 1978, J. Chem. Phys. 82, 1192.
- Van Zee, R.J., R.F. Ferrante, K.J. Zeringue and W. Weltner, 1981, J. Chem. Phys. 75, 5297.
- Van Zee, R.J., S. Li and W. Weltner, 1994, J. Chem. Phys. 100, 4010.
- Veillard, A., ed., 1986, Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry, NATO ASI Series, Series C, Vol. 176 (Reidel, Dordrecht).
- Visscher, L., 1993, Relativity and electron correlation in chemistry, Thesis (University of Groningen, Netherlands).
- Visscher, L., T. Saue, W.C. Nieuwpoort, K. Faegri and O. Gropen, 1993, J. Chem. Phys. 99, 6704.
- Visscher, L., O. Visser, P.J.C. Aerts, H. Merenga and W.C. Nieuwpoort, 1994, Comput. Phys. Commun. 81, 120.
- Visser, O., 1992, Relativity in quantum chemistry with applications to group IV hydrides and EuO⁶₆, Thesis (University of Groningen, Netherlands).
- Visser, O., P.J.C. Aerts, D. Hegarty and W.C. Nieuwpoort, 1987, Chem. Phys. Lett. 134, 34.
- Visser, O., L. Visscher, P.J.C. Aerts and W.C. Nieuwpoort, 1992a, Theor. Chim. Acta 81, 405.
- Visser, O., L. Visscher, P.J.C. Aerts and W.C. Nieuwpoort, 1992b, J. Chem. Phys. 96, 2910.
- Visser, R., J. Andriessen, P. Dorenbos and C.W.E. Eijk, 1993, J. Phys.: Condens. Matter 5, 5887.
- Von Arnim, M., 1993, Theor. Chim. Acta 87, 41.

- Von Arnim, M., and S.D. Peyerimhoff, 1993, Chem. Phys. Lett. 210, 488.
- Vosko, S.H., L. Wilk and M. Nusair, 1980, Can. J. Phys. 58, 1200.
- Waber, J.T., and D.T. Cromer, 1965, J. Chem. Phys. 42, 4116.
- Wadt, W.R., 1981, J. Am. Chem. Soc. 103, 6053.
- Wadt, W.R., 1982, Chem. Phys. 89, 245.
- Wadt, W.R., and P.J. Hay, 1985, J. Chem. Phys. 82, 284.
- Wallmeier, H., and W. Kutzelnigg, 1981, Chem. Phys. Lett. 78, 341.
- Walsh, A.D., 1953, J. Phys. Soc., p. 2266.
- Wang, S.G., and W.H.E. Schwarz, 1995, J. Phys. Chem. 99, 11687.
- Wang, S.G., D.K. Pan and W.H.E. Schwarz, 1995, J. Chem. Phys. 102, 9296.
- Warren, K.D., 1975, Inorg. Chem. 14, 3095.
- Weber, J., H. Berthou and C.K. Jørgensen, 1977a, Chem. Phys. Lett. 45, 1.
- Weber, J., H. Berthou and C.K. Jørgensen, 1977b, Chem. Phys. 26, 69.
- Weeks, J.D., A.U. Hazi and S.A. Rice, 1969, Adv. Chem. Phys. 16, 283.
- Wijesundera, W.P., S.H. Vosko and F.A. Parpia, 1995, Phys. Rev. A 51, 278.
- Wilson, S., ed., 1988a, Relativistic Effects in Atoms and Molecules, Methods in Computational Chemistry, Vol. 2 (Plenum, New York).
- Wilson, S., 1988b, Relativistic molecular structure

calculations, in: Relativistic Effects in Atoms and Molecules, Methods in Computational Chemistry, Vol. 2, ed. S. Wilson (Plenum, New York).

- Wolfsberg, M., and L. Helmholz, 1952, J. Chem. Phys. 20, 837.
- Wood, J.H., and A.M. Boring, 1978, Phys. Rev. B 18, 2701.
- Xu, G., and J. Ren, 1986, Int. J. Quantum Chem. 29, 1017.
- Xu, G., and J. Ren, 1987, Lanthanide Actinide Res. 2, 67.
- Yadav, B.R., S.B. Rai and D.K. Rai, 1981, J. Mol. Spectrosc. 89, 1.
- Yang, C.Y., 1983, Relativistic scattered-wave calculations for molecules and clusters in solids, in: Relativistic Effects in Atoms, Molecules and Solids, NATO ASI Series, Series B: Physics, Vol. 87, ed. G.L. Malli (Plenum, New York) p. 335.
- Yokozeki, A., and M. Menzinger, 1976, Chem. Phys. 14, 427.
- Zhang, Q.L., S.C. O'Brien, J.R. Heath, Y. Liu, R.F. Curl, H.W. Kroto and R.E. Smalley, 1986, J. Phys. Chem. 90, 525.
- Ziegler, T., J.G. Snijders and E.J. Baerends, 1980, Chem. Phys. Lett. 75, 1.
- Ziegler, T., J.G. Snijders and E.J. Baerends, 1981, J. Chem. Phys. 74, 1271.
- Ziegler, T., V. Tschinke, E.J. Baerends, J.G. Snijders and W. Ravenek, 1989, J. Phys. Chem. 93, 3050.

AUTHOR INDEX

Abbas, Y. 413, 418 Abdulsabirov, R.Yu. 336, 350, 357, 364, 433 Abdulsabirov, R.Yu., see Al'tshuler, S.A. 354, 434, 435 Abella, I.D., see Kurnit, N.A. 526, 531 Abragam, A. 297, 298, 308, 310, 343, 363, 367, 371, 384, 385, 401–403, 406 Abragam, A., see Chapellier, M. 401 Abraham, M.M. 445 Abraham, M.M., see Loong, C.-K. 318, 319, 321, 322 Abraham, M.M., see Rappaz, M. 392 Achiba, Y., see Nagase, S. 699, 717 Ackermann, R.J. 651, 666 Adachi, H., see Kobayashi, H. 610, 700, 701 Adachi, H., see Rosén, A. 700 Adachi, K., see Amako, Y. 158-160 Adler, D.L. 598 Adroja, D.T., see Sinha, V.K. 215, 218 Aeppli, G., see Reich, D.H. 458, 469-471 Aeppli, G., see Rosenbaum, T.F. 458 Aeppli, G., see Wu, W. 458, 469 Aeppli, G., see Youngblood, R.W. 468 Aerts, P.J.C. 635 Aerts, P.J.C., see Broer, R. 612 Aerts, P.J.C., see DeJong, W.A. 635, 707 Aerts, P.J.C., see Nieuwpoort, W.C. 635, 636 Aerts, P.J.C., see Visscher, L. 635 Aerts, P.J.C., see Visser, O. 613, 614, 631, 632, 706-710, 712, 716 Aggarwal, K., see Gal, J. 150, 154, 174, 176-178, 185, 201 Aharony, A. 36, 70, 424 Aharony, A., see Goldschmidt, Y.Y. 36, 70 Aharony, A., see Rohrer, H. 468 Ahlers, G. 424, 425 Ahlheim, U., see Geibel, C. 154, 183 Ahlheim, U., see Rauchschwalbe, U. 178, 181-183, 195 Ahn, B.T., see Beyers, R. 474, 475 Ahrens, R., see Schreiner, Th. 489 Aizenberg, I.B., see Malkin, B.Z. 314 Akasaka, T., see Kobayashi, K. 718 Akayama, M. 215 Akayama, M., see Sun, H. 258, 259

Alascio, B.R., see Aligia, A.A. 473 Albert, J., see Kitagawa, T. 600 Albston, S.D., see van Dover, R.B. 94 Aldred, A.T. 304 Aleksandrov, I.V. 435 Aleonard, S. 305 Alford, J.M., see Chai, Y. 696, 699 Alford, M.J., see Guo, T. 696 Algarabel, P.A. 228 Algarabel, P.A., see Arnold, Z. 228, 252 Algarabel, P.A., see Garcia, L.M. 215 Algarabel, P.A., see Moze, O. 228, 248 Algarabel, P.A., see Pareti, L. 228, 229, 232, 244, 245, 248 Aligia, A.A. 473 Allain, J.Y. 587, 591, 592 Allain, J.Y., see Ronarc'h, D. 537, 588 Allen, H. 521, 523-525 Allen, R., see Kintz, G.J. 557 Allenspach, P. 318, 323, 413, 422, 479 Allenspach, P., see Guillaume, M. 318, 323, 473 Allenspach, P., see Mesot, J. 323, 475, 478 Allenspach, P., see Podlesnyak, A. 318 Alloul, H., see Brom, H. 485 Allsop, A.L. 401 Allsop, A.L., see Clark, R.G. 401 Allsop, A.L., see Suzuki, H. 400, 401 Almeida, M., see Gonçalves, A.P. 148, 169, 268, 269, 272, 286 Almeida, M., see Paixão, J.A. 177, 178, 202, 286 Almloef, J. 638 Almloef, J., see Park, C. 689 Als-Nielsen, J. 302, 413, 424 Als-Nielsen, J., see Holmes, L.M. 346, 420 Als-Nielsen, J., see Kjaer, K. 458, 470 Altounian, Z., see Liao, L.X. 261 Al'tshuler, S.A. 297, 298, 308, 310, 350, 352-356, 361-365, 374, 377, 378, 382, 386, 389, 400, 434, 435, 444, 450 Amako, Y. 158-160 Amelinckx, S., see Reyes-Gasga, J. 474, 475, 478 Ames, L.L. 660 Aminov, L.K. 298-300, 312, 363, 366, 368, 372, 377, 379, 381, 383, 384, 388, 390, 392, 393,

Aminov, L.K. (cont'd) 396, 397, 399, 441, 445. 448, 452, 454, 455, 461, 469, 483 Amoretti, G., see Moze, O. 209, 210, 272 Anagnostou, M.S. 263 Anagnostou, M.S., see Christides, C. 209, 228, 253 Anders, A.G. 408, 421 Andersen, N.H., see Zeiske, T. 475 Anderson, P.W., see Klauder, J.R. 486 Anderson, R.J. 346 Andrade, A.V.M. 651, 704, 705, 717 Andrae, D. 647 Andreev, A.V. 148, 154, 156, 202, 215, 221, 222, 245-250, 267-270, 274-276, 283-286 Andreev, A.V., see Vagizov, F.G. 268, 283-285 Andreev, S.V., see Andreev, A.V. 156, 267, 269 Andreoni, W., see Laasonen, K. 699 Andres, K. 400, 414 Andres, K., see Bucher, E. 305 Andriessen, J. 714, 716 Andriessen, J., see Visser, R. 710, 712, 713, 716 Andronenko, S.I. 322, 359, 391 Andronenko, S.I., see Ioffe, V.A. 359, 360 Andronenko, S.I., see Pekurovskii, V.R. 322, 324 Antipin, A.A. 382, 384, 385, 390, 392, 393 Arbaboff, E., see Gal, J. 150, 154, 174, 176-178, 185, 201 Arbaboff, E., see Halevy, I. 186-189, 202 Armbruster, A. 351 Armstrong, R.L., see Morra, R.M. 428 Arnold, Z. 228, 252 Arrechi, F.T. 530 Artigaud, S., see Marcerou, J.F. 588 Aruge Katori, H., see Andreev, A.V. 267 Asano, H., see Tanabe, K. 487, 488 Asano, S. 259 Asano, S., see Ishida, S. 258 Asawa, C.K. 567 Asch, L., see Gal, J. 163, 165, 177, 181, 182 Assmus, W., see Frowein, R. 425 Asta, M., see Fontaine, D. 473 Asti, G. 243, 270 Aszmus, W., see Kotzler, J. 405 Atashroo, T., see LaJohn, L.A. 646 Atashroo, T., see Ross, R.B. 646 Atsarkin, V.A. 384 Attenkofer, K. 114, 115 Aukhadeev, F.L. 351, 353, 357, 368, 377, 382, 431, 435, 439 Aukhadeev, F.L., see Al'tshuler, S.A. 354, 377, 382, 434, 435, 444 Aukhadeev, F.L., see Egorov, A.V. 400 Aukhadeev, F.L., see Zhdanov, R.Sh. 367

Auzel, F. 510, 511, 532-535, 538-540, 542-546, 548, 550, 552, 556-561, 563-568, 570-574, 576-578, 581, 583-586, 588, 592, 593, 595, 598, 599 Auzel, F., see Bonneville, R. 557 Auzel, F., see Budin, J.P. 566 Auzel, F., see Chen, Y.H. 563, 564, 593 Auzel, F., see Deutschbein, O.K. 510 Auzel, F., see Dexpert-Ghys, J. 538, 539, 549 Auzel, F., see Gouedard, C. 538, 539 Auzel, F., see Hubert, S. 534, 535 Auzel, F., see Malta, O.L. 600 Auzel, F., see Michel, J.C. 575 Auzel, F., see Pouradier, J.F. 551, 552 Auzel, F., see Ronarc'h, D. 537, 588 Auzel, F., see Santa-Cruz, P.A. 578, 599 Auzel, F., see Sheperd, D.P. 600 Auzel, F., see Zhou, B.W. 598 Avanesov, A.G. 323, 324 Averill, F.W., see Rosén, A. 700 Axe, J.D. 317, 552 Axe, J.D., see Bohr, J. 30, 54 Axe, J.D., see Gibbs, D. 6, 10, 13, 16 Axe, J.D., see Youngblood, R.W. 468 Axmann, A., see Ennen, H. 594 Aylesworth, K.D., see Harris, V.G. 119, 140 Aylesworth, K.D., see Shan, Z.S. 107 Aylesworth, K.D., see Zhao, Z.R. 265 Ayoma, T., see Matsuoka, O. 635 Baak, J. 489 Babizhet'sky, V.S., see Stelmakhovich, B.M. 146, 154 Bachelet, G.B. 646, 699 Bacmann, M., see Tomey, E. 237 Baczewski, C.T. 119 Bader, S.D., see Falicov, L.M. 20, 32, 35, 47 Badía, F. 110 Badry, M.A., see Badía, F. 110 Badurski, D., see Suski, W. 185, 268, 272, 282, 283 Baeck, K.K. 635 Baerends, E.J. 617 Baerends, E.J., see Boerrigter, P.M. 691 Baerends, E.J., see DeKock, R.L. 684, 688, 716 Baerends, E.J., see Pyykkö, P. 619 Baerends, E.J., see Schwarz, W.H.E. 615, 617 Baerends, E.J., see Snijders, J.G. 641, 659, 667, 680 Baerends, E.J., see Van Lenthe, E. 638 Baerends, E.J., see Ziegler, T. 619, 684, 688 Baetzold, R.C., see Islam, M.S. 475, 476 Bagus, P.S. 626, 627 Bagus, P.S., see Broer, R. 612

Bakar, A., see Sysa, L.V. 146 Baker, J.E., see Rothman, S.J. 475 Baker, J.M. 329, 343, 391, 444, 456 Baker, J.M., see Abraham, M.M. 445 Baker, J.M., see Anderson, R.J. 346 Bakharev, O.N. 318, 323, 472, 479, 481-483, 486-491 Bakharev, O.N., see Ishigaki, T. 318, 323 Bakharev, O.N., see Teplov, M.A. 479, 487, 489 Bakker, K., see Haije, W.G. 149, 152, 157, 228, 248 Balasubramanian, K. 612-614, 617, 658, 660, 691, 697 Balasubramanian, K., see Christiansen, P.A. 613, 648 Balasubramanian, K., see Das, K.K. 658, 716 Ball, G.A. 600 Ballard, R.L., see King, A.R. 456 Ballestracci, R. 418 Baran, A. 148, 152-154, 163, 165, 167, 177, 178, 181, 188-190, 194, 195, 267, 268, 271, 273 Baran, A., see Bourée-Vigneron, F. 150, 152, 163, 165, 167-169 Baran, A., see Drulis, M. 181, 183 Baran, A., see Ptasiewicz-B, ak, B. 150, 176, 177, 181-183, 190, 194, 195 Baran, A., see St, epień-Damm, J. 148, 152, 169, 177 Baran, A., see Suski, W. 148, 154, 155, 181, 184, 185, 267, 268, 271, 272, 277-279, 281, 283 Baran, A., see Wysłocki, J.J. 246, 267, 268, 271 Baran, A., see Zeleny, M. 162, 200, 267, 268, 273 Barandiarán, Z. 639, 644 Barandiarán, Z., see Huzinaga, S. 644 Barandiarán, Z., see Seijo, L. 644 Baraniak, V.M., see Sysa, L.V. 146 Baranov, N.V., see Andreev, A.V. 267-270, 275 Bardsley, J.N. 646 Barnes, R.G. 301, 318, 323 Barrière, A.S. 600 Barrow, R.F. 679 Barrow, R.F., see Dulick, M. 660-662, 666, 667, 669-674, 676 Barrow, R.F., see Linton, C. 667, 668 Bartashevich, M.I., see Andreev, A.V. 148, 215, 248, 267 Bartashevich, M.I., see Kudrevatykh, N.V. 249 Barthelat, J.C. 640, 646 Barthelat, J.C., see Durand, P. 646 Barthelat, J.C., see Teichteil, C.H. 613 Bartolomé, J., see Garcia, L.M. 215, 237-239, 246, 247, 252 Bartolomé, J., see Luis, F. 237, 238, 252

Basch, H., see Stevens, W.J. 647 Bates, S. 13 Batlogg, B., see Cava, R.J. 474, 475 Batterman, B.W., see Vettier, C. 46 Battison, J.E. 300, 366, 404 Baud, G., see Vedrine, A. 305 Baudelet, F. 114 Baudelet, F., see Tolentino, H. 486 Baudry, A., see Luche, M.C. 21, 61, 64, 65 Bauer, Ph., see Cherifi, K. 109-111 Baxter, E., see Boudreaux, E.A. 695 Bayart, D., see Clescla, B. 588 Baybutt, P., see Kahn, L.R. 639, 646 Bayreuther, G., see O'Grady, K. 126-128 Bazan, C., see Ioffe, V.A. 359, 360 Bazhan, A.N., see Andronenko, S.I. 322, 359 Bazhan, A.N., see Ioffe, V.A. 359, 360 Beach, R.S. 11, 21, 22, 24, 25, 30, 45, 46, 57, 59, 61, 62, 65 Beach, R.S., see Salamon, M.B. 3, 46, 48, 52, 70 Beach, R.S., see Tsui, F. 65 Beall, W., see Fowler, W.B. 542 Beattie, I.R. 686, 687 Beaufils, J.C., see Dulick, M. 676 Beauvillain, P. 321, 346, 413, 420, 424, 425, 468 Beauvillain, P., see Magarino, J. 426, 444 Beauvillain, P., see Mennenga, G. 458, 468, 469 Becher, W. 346, 413 Becke, A.D. 641, 659, 667, 680, 700 Becker, P.C. 511, 537, 580, 588 Becker, P.C., see Desurvire, E. 587 Becker, P.J. 413, 429 Bednorz, J.G. 478 Bednorz, J.G., see D'Iorio, M. 365 Belanger, D.P., see Reich, D.H. 458, 469-471 Bellesis, G.H. 413 Bellesis, G.H., see Simizu, S. 413, 418 Belov, K.P. 298, 413 Belozerov, E.V., see Ermolenko, A.S. 154, 155, 207, 209, 233, 234, 237, 249, 250 Belozerov, Ye.V., see Scherbakova, Ye.V. 237, 238, 248 Bender, C.F. 610, 685 Benett, L.H., see Melamud, M. 151, 157 Bennahmias, M., see Rosov, N. 413 Bennett, K.B., see Grubb, S.G. 592 Bennington, S.M., see Podlesnyak, A. 318 Beno, M., see Dunlap, B.D. 413 Benyattou, T. 596 Berezyuk, D.A. 147, 148, 233, 234, 237, 240, 242, 243 Berezyuk, D.A., see Bodak, O.I. 157 Berg, R.A. 665 Bergersen, B., see Xu, H.-J. 418

Bergner, A. 647 Berkowitz, J., see Ruščić, B. 610, 641, 685, 686 Berlinger, W., see D'Iorio, M. 365 Berlureau, T. 157, 267, 268, 272, 277, 278, 281 Berlureau, T., see Wang, Xian-zhong 194, 197 Bernard, A. 661, 673 Berndts, P., see Kasten, A. 413 Bertaut, E.F., see Ballestracci, R. 418 Berthelou, L., see Clescla, B. 588 Berthou, H., see Weber, J. 610, 706 Bertolini, G., see Greco, A. 689 Berton, A., see Rossat-Mignod, J. 413, 418 Bertram, H.N. 132 Bertrand, C., see Le Roy, J. 263 Besse, J.P., see Vedrine, A. 305 Bethe, H.A. 321, 629 Bethune, D.S., see Johnson, R.D. 699 Beveridge, D.L., see Pople, J.A. 649 Beyers, R. 474, 475 Beylat, J.L., see Clescla, B. 588 Beznosov, A.B. 150, 273 Bier, K.D., see Kirkwood, A.D. 681 Bierig, R.W., see Rimai, L. 387, 392 Bilsdean, F., see Kitagawa, T. 600 Bingham, D. 319, 458, 459, 467 Birgeneau, R.J. 365 Birgeneau, R.J., see Anderson, R.J. 346 Birgeneau, R.J., see Cohen, E. 365 Birgeneau, R.J., see Hutchings, M.T. 343 Birgeneau, R.J., see Lyons, K.B. 365 Bischoff, H. 322 Bist, H.D., see Malhotra, V.M. 392 Bitko, D., see Wu, W. 458, 469 Björk, G., see Yamamoto, Y. 527 Blackstead, H.A. 478 Blaise, J. 612 Blasse, G. 599 Blasser, S., see Reimer, P.M. 16 Bleaney, B. 298, 301, 318, 322, 343, 349, 351, 363, 364, 366-368, 372, 373, 387, 390, 392, 400, 401, 408, 413, 416, 429, 444 Bleaney, B., see Abragam, A. 297, 298, 308, 310, 343, 363, 367, 371, 385, 402, 406 Bleaney, B., see Abraham, M.M. 445 Bleaney, B., see Allsop, A.L. 401 Bleaney, B., see Baker, J.M. 444 Bleaney, B., see Bingham, D. 319 Bleaney, B., see Suzuki, H. 400, 401 Blixt, P. 593 Bloch, F. 379 Bloch, F., see Wangsness, R.K. 379 Bloembergen, N. 379 Blöte, H.W.J. 413 Blöte, H.W.J., see Lagendijk, E. 408, 413

Blount, E.I., see Cohen, E. 365 Blount, E.I., see Lyons, K.B. 365 Blumberg, W.E. 487 Blume, M. 639 Blume, M., see Sternheimer, R.M. 314 Blumen, A., see Klafter, J. 488 Boatner, L.A., see Loong, C.-K. 318, 319, 321, 322 Boatner, L.A., see Rappaz, M. 392 Boccara, A.C. 578 Bodak, O.I. 157 Bodak, O.I., see Berezyuk, D.A. 147, 148, 233, 234, 237, 240, 242, 243 Bodak, O.I., see Gladyshevsky, E.I. 146-148, 154, 156, 206 Bodak, O.I., see Sokolovskava, E.M. 157 Boender, G.J., see Gubbens, P.C.M. 215, 232, 233 Boerrigter, P.M. 691 Bogatkin, A.N., see Andreev, A.V. 221, 222, 245, 246, 249, 250 Bogatova, T.B., see Aminov, L.K. 390, 392, 393 Boggis, J.M. 588 Bogomolova, G.A. 317 Bohm, W. 322 Bohr, J. 30, 54 Bohr, J., see Gibbs, D. 13 Bohr, J., see Kwo, J. 21, 22, 30 Bohr, J., see Majkrzak, C.F. 3, 46, 48, 54, 65 Bojarczuk, N.A., see Cadieu, F.J. 215 Bol'shakov, I.G., see Al'tshuler, S.A. 363, 365, 386 Boltich, E.B., see Cheng, S.F. 218 Boltich, E.B., see Zhang, L.Y. 248, 249 Bolzoni, F.J., see Asti, G. 270 Bondar', I.A. 355, 356, 359, 360 Bondar', I.A., see Andronenko, S.I. 359 Bondar', I.A., see Ioffe, V.A. 359, 360 Bonfait, G., see Gonçalves, A.P. 148, 169, 268, 269, 272, 286 Bonfait, G., see Paixão, J.A. 177, 178, 202, 286 Böni, P., see Kwo, J. 21, 22, 30 Böni, P., see Majkrzak, C.F. 46 Bonifacic, V. 639, 644 Bonifacio, R. 512, 524, 526-528, 530 Bonneville, R. 557 Bonrath, H. 413 Bonsall, L. 333, 341 Bonville, P., see Hodges, J.A. 475, 483, 485 Borchers, A., see Salamon, M.B. 3, 14, 21, 39, 46.48 Borchers, J.A. 11, 24, 30, 42, 46, 55, 57, 58 Borchers, J.A., see Beach, R.S. 21, 22, 24, 25, 30, 45, 46, 57, 59, 62

734

Borchers, J.A., see Erwin, R.W. 40, 41, 44, 46, 48, 52, 54 Borchers, J.A., see Everitt, B.A. 10, 14, 25, 65 Borchers, J.A., see Flynn, C.P. 47 Borchers, J.A., see Gibbs, D. 6, 10, 13, 16 Borchers, J.A., see Rhyne, J.J. 46, 48, 49, 51, 52 Borchers, J.A., see Salamon, M.B. 3, 46, 48, 52, 70 Borchers, J.A., see Tanaka, Y. 25, 30, 31 Borchers, J.A., see Tsui, F. 65, 66, 68 Borel, C., see Sheperd, D.P. 600 Borghini, M. 385 Boring, A.M. 640, 690, 715 Boring, A.M., see Wood, J.H. 617, 639 Born, M. 315, 337, 629 Borodi, G., see Coldea, M. 167, 168, 181 Bouchiat, H., see Caudron, R. 10 Boudreaux, E.A. 695 Bouffard, V., see Roinel, Y. 386 Bourée-Vigneron, F. 150, 152, 163, 165, 167-169 Bowden, G.J., see Allsop, A.L. 401 Bowden, G.J., see Clark, R.G. 401 Bowden, G.J., see Suzuki, H. 400, 401 Bower, J.E., see Kwo, J. 3, 14, 20, 39, 47 Boyd, R.W., see Malcuit, M.S. 528, 532 Boyer, P., see Luche, M.C. 21, 61, 64, 65 Brabers, J.H.V.J. 228, 229 Brabers, J.H.V.J., see Zhao, Z.G. 135 Bradbury, M.I. 313 Braden, M., see Schweiss, P. 484 Brand, R.A., see Badía, F. 110 Brand, R.A., see Scholz, B. 109, 111, 112 Brände, H. 150, 270 Brandel, V. 577 Bratsberg, H., see Ellingsen, O.S. 346, 413, 417 Brauchle, G., see Riedling, S. 478 Braunisch, W. 478 Brede, R. 591 Bredikhin, S.I. 477 Breit, G. 631 Brenton, J.L., see Adler, D.L. 598 Breteau, J.M., see Li, M.J. 580, 599 Brewer, R.G., see De Voe, R.G. 531 Brewer, R.G., see Genack, A.Z. 531 Brezin, E. 424 Bridenbaugh, P.M., see Peterson, G.E. 567 Brierley, M.C. 588 Brierley, M.C., see Whitley, T.J. 592 Brierley, S.K. 468 Briggs, G.A., see Bleaney, B. 351, 387 Brinkmann, D. 475 Brinkmann, J. 425 Briskina, C.M., see Markushev, V.M. 538 Broach, R.W. 302, 303, 370, 448

Brodsky, M.B., see Gibbs, D. 13 Brodsky, M.B., see Grünberg, P. 39 Broer, R. 612 Brom, H. 485 Brom, H.B., see Baak, J. 489 Brom, H.B., see Bakharev, O.N. 479, 488, 489 Brom, H.B., see Teplov, M.A. 487, 489 Brom, H.B., see Veenendaal, E.J. 305, 366, 367, 413 Brommer, P.E., see Kim-Ngan, N.H. 168 Brooks, M.S.S., see Lander, G.H. 150 Brooks, M.S.S., see Trygg, J. 157, 160, 161, 257 Brorson, S.D. 600 Brouder, C., see Baudelet, F. 114 Brouha, M., see Buschow, K.H.J. 209, 210, 215, 228, 232, 237, 241, 269, 273 Brown, A.J., see Caudron, R. 10 Brown, G.E. 636 Brown, P.J. 413, 416 Bruesch, P., see Furrer, A. 318, 323, 422, 475 Bruggink, W.H.M., see Reyes-Gasga, J. 474, 475, 478 Bruno, P. 69 Brunton, G.D., see Thoma, R.E. 302 Bruson, A., see Cherifi, K. 109-111 Buchal, C., see Folle, H.R. 400 Buchal, Ch., see Kubota, M. 400 Bucheler, A., see Berg, R.A. 665 Bucher, B., see Wachter, P. 490 Bucher, E. 305 Bucher, E., see Andres, K. 400 Buchgeister, M., see Clinton, T.W. 422 Buchgeister, M., see Heinmaa, I. 475 Buchgeister, M., see Krekels, T. 478 Buchholz, D.B., see Mogilevsky, R. 489 Buchmeister, M., see Clinton, T.W. 422 Buckmaster, H.A., see Smith, M.R. 392 Budin, J.P. 566 Budzyński, M., see Stefański, P. 209 Buisson, R., see Vial, J.C. 559 Bulaevskii, L.N. 478 Bulman, J.B. 413 Bumagina, L.A. 323, 324, 352, 415, 431, 434 Bumagina, L.A., see Al'tshuler, S.A. 354, 434, 435 Bumagina, L.A., see Bogomolova, G.A. 317 Buntschuh, B.M., see Vettier, C. 46 Burbank, R.D., see Cohen, E. 365 Burlet, P., see Paixão, J.A. 177, 178, 202, 286 Burns, G., see Axe, J.D. 317 Burriel, R., see Garcia, L.M. 237-239, 246, 247, 252 Burriel, R., see Luis, F. 237, 238, 252 Burrus, C.A., see Stone, J. 580

Burshtein, A.I. 377 Bursten, B.E., see Pepper, M. 609, 613, 691 Bursten, B.E., see Strittmatter, R.J. 690 Burzo, E. 146, 202, 203, 205, 206 Buschow, K.H.J. 148, 152-157, 165, 167, 169, 174-178, 181, 207, 209, 210, 215, 228-230, 232, 237, 241, 248, 249, 269, 271, 273 Buschow, K.H.J., see Brabers, J.H.V.J. 228, 229 Buschow, K.H.J., see de Boer, F.R. 228, 255 Buschow, K.H.J., see de Mooij, D.B. 148, 156, 209, 215, 222, 228, 232, 234, 237, 241 Buschow, K.H.J., see Denissen, C.J.M. 161, 228, 257 Buschow, K.H.J., see Dirken, M.W. 157, 215, 228, 241, 243 Buschow, K.H.J., see Grössinger, R. 228, 246 Buschow, K.H.J., see Gubbens, P.C.M. 209, 215, 228, 232, 233, 253, 257, 275 Buschow, K.H.J., see Haije, W.G. 149, 152, 157, 228, 248 Buschow, K.H.J., see Helmholdt, R.B. 149, 156, 228, 255 Buschow, K.H.J., see Moze, O. 157, 165, 167, 168, 176, 209, 210, 272 Buschow, K.H.J., see Sinnemann, Th. 209, 215, 228, 241 Buschow, K.H.J., see van der Kraan, A.M. 148 Buschow, K.H.J., see van Engelen, P.P.J. 150, 270 Buschow, K.H.J., see Verhoef, R. 149, 156, 215, 228, 232, 233, 237, 241, 246, 257 Buschow, K.H.J., see Yang, F.-M. 232, 233, 248, 249 Buschow, K.H.J., see Zhao, Z.G. 135 Butscher, W., see Esser, M. 635, 648 Buyers, W., see Graham, J.T. 459 Buyers, W.J.L., see Rebelsky, L. 272 Cable, J.W. 14 Cable, J.W., see Kwo, J. 21, 22, 30 Cable, J.W., see Majkrzak, C.F. 39, 44, 46-48, 60 Caciuffo, R., see Gal, J. 181, 182 Caciuffo, R., see Moze, O. 165, 167, 168, 209, 210, 272 Cadieu, F.J. 215, 264 Cadieu, F.J., see Hegde, H. 146, 160, 161 Cadieu, F.J., see Kamprath, N. 264, 266 Cadieu, F.J., see Liu, N.C. 264 Cadieu, F.J., see Navarathna, A. 160 Cadogan, J.M. 203, 228 Cadogan, J.M., see Wang, Xian-zhong 194, 197 Cai, Z. 613, 651, 652 Callen, E. 137, 138 Camley, R.E. 20, 65 Campbell, I.A., see Suzuki, H. 400, 401

Cannelli, G. 477 Cannon, R.S., see Grubb, S.G. 592 Cantelli, R., see Cannelli, G. 477 Cao, G., see Bulman, J.B. 413 Cao, G., see Cao, Y. 705 Cao. L. 215 Cao, X.W., see Tang, Y.J. 413, 420 Cao, Y. 705 Capehart, T.W. 234 Capel, H.W. 408 Capestan, M., see Vedrine, A. 305 Capitán, M.J., see Márquez, A. 665, 716 Car, R. 699 Cardona, M., see Hadjiev, V.G. 476, 489 Cardona, M., see Iliev, M. 475 Carette, P. 660, 665-667, 669, 671, 673, 676 Carette, P., see Linton, C. 667, 668 Cargill III, G.S., see Mizoguchi, T. 120, 125 Carlnäs, J., see Blixt, P. 593 Carlson, J.W., see Funk, D.S. 599 Carlson, N.W. 536 Carretta, P. 485 Carter, J.N. 590 Carter, J.N., see Lauder, R.D.T. 590 Carter, S., see Bredikhin, S.I. 477 Carter, S.F., see Carter, J.N. 590 Carter, S.F., see Smart, R.G. 592 Casalta, H., see Schleger, P. 486 Case, D.A. 610, 641, 706 Case, W.E. 561 Case, W.E., see Chivian, J.S. 511 Case, W.E., see Koch, M.E. 564, 593 Case, W.E., see Kueny, A.W. 561, 562 Cashion, J.D. 346, 408, 413 Cashion, J.D., see Bingham, D. 458, 459, 467 Catanese, C.A. 343, 346, 413 Catanese, C.A., see Skjeltorp, A.T. 346, 413 Caudron, R. 10 Cava, R.J. 474, 475 Cavigan, J.P., see Hu, B.-P. 148, 215, 251 Ceder, G., see Fontaine, D. 473 Cesca, S., see Greco, A. 689 Chai, B., see Brede, R. 591 Chai, Y. 696, 699 Chai, Y., see Guo, T. 696 Chambaz, B., see Pelenc, D. 600 Chan, K.S. 338, 358 Chandra, P. 637 Chang, A.H.H. 613, 648, 649, 658, 677, 691, 697, 698, 717 Chang, A.H.H., see Dolg, M. 629, 648, 692-694, 716 Chang, C. 638 Chang, L.L. 15

736

Chang, R.P.H., see Mogilevsky, R. 489 Chang, R.S.F., see Scott, B.P. 591 Chang, T.-C. 643, 644 Chang, W.C., see Chin, T.S. 209, 215, 228, 232, 237 Chang, W.C., see Huang, S.H. 263 Chang, Y.-C., see Xia, J.-B. 70 Chantrell, R.W., see Lyberatos, A. 130 Chapellier, M. 401 Chappert, C., see Beauvillain, P. 424, 425, 468 Chappert, C., see Bruno, P. 69 Charasse, M.N. 594 Charasse, M.N., see Benyattou, T. 596 Charkin, O.P., see Kaupp, M. 716 Chartier, I. 600 Chartier, I., see Pelenc, D. 600 Chasanov, M.G., see Gabelnick, S.D. 670, 671, 673, 684 Chater, R.J., see Bredikhin, S.I. 477 Chatterjee, R., see Smith, M.R. 392 Chatterji, A., see Neogy, D. 323 Chaussy, J., see Rossat-Mignod, J. 413, 418 Chavignon, J., see Auzel, F. 588 Chazelas, J., see Charasse, M.N. 594 Chełkowska, G. 194, 195 Chełkowska, G., see Chełkowski, A. 194, 195 Chełkowska, G., see Jelonek, J. 194, 195 Chełkowski, A. 148, 169, 174-176, 194, 195 Chełkowski, A., see Chełkowska, G. 194, 195 Chełkowski, A., see Jelonek, J. 194, 195 Chen, K., see Cadieu, F.J. 264 Chen, K., see Hegde, H. 146, 160, 161 Chen, S.C., see Chan, K.S. 338 Chen, S.K., see Huang, S.H. 263 Chen, T.G., see Xie, X.M. 475 Chen, W., see Li, Z. 610, 705 Chen, X., see Geng, M.M. 237 Chen, Y.C., see Guan, W.Y. 413 Chen, Y.H. 563, 564, 593 Chen, Y.H., see Auzel, F. 563, 592 Chen, Y.S., see Huang, S.H. 263 Chen, Z.D., see O'Shea, M.J. 125 Cheng, B.P., see Yang, Y.-C. 215, 243, 245 Cheng, S.F. 218 Cheng, S.F., see Sinha, V.K. 215, 216, 218, 219, 221, 222, 248 Cheng, X., see Sun, L. 477 Cheong, S.-W., see Hundley, M.F. 413 Cheong, S.-W., see Skanthakumar, S. 413 Cherifi, K. 109-111 Chermette, H., see Gérard, I. 715, 716 Chernov, K.P., see Korableva, S.L. 387 Cherny, A.S., see Khat'sko, E.N. 413 Cherny, A.S., see Pshisukha, A.M. 413

Chesler, R.B., see Singh, S. 538 Chevalier, B., see Berlureau, T. 157, 267, 268, 272, 277, 278, 281 Chevalier, B., see Matar, S.F. 270, 286 Chevalier, B., see Wang, Xian-zhong 194, 197 Chiang, C., see Hamann, D.R. 646 Chibante, L.P.F., see Chai, Y. 696, 699 Chien, C.L., see Bohr, J. 30, 54 Chien, C.L., see Camley, R.E. 20, 65 Chien, C.L., see Kwo, J. 21, 22, 30 Chien, C.L., see Majkrzak, C.F. 3, 46, 48, 54, 65 Chin, T.S. 209, 215, 228, 232, 237 Chin, T.S., see Huang, S.H. 263 Chinn, S.R., see Hong, H.Y. 569 Chirkin, Yu.K., see Antipin, A.A. 392, 393 Chistyakov, D.D., see Jurczyk, M. 228, 229, 231, 233, 246 Chivian, J.S. 511 Chocholaes, H., see Kubota, M. 400 Choi, J.S., see Kikuchi, R. 473 Chojinicki, A.H., see Barrow, R.F. 679 Christensen, H.P. 318, 319, 321, 323 Christiansen, P.A. 612, 613, 646-648 Christiansen, P.A., see Ermler, W.C. 612, 613. 646 Christiansen, P.A., see Hurley, M.M. 646 Christiansen, P.A., see LaJohn, L.A. 646 Christiansen, P.A., see Pacios, L.F. 646 Christiansen, P.A., see Ross, R.B. 646 Christides, C. 209, 215, 228, 234, 237, 248-250, 253, 259, 261, 273 Chrosch, J. 474, 475 Chrysochoos, J. 568 Chu, S.Y., see Schwarz, W.H.E. 62.0 Chuang, Y.C., see Huang, R.-W. 253 Chudnovsky, E.M. 70 Chung, R., see Caudron, R. 10 Ciliberto, E., see Streitwieser, A. 610, 689, 691 Citrin, P.H., see Adler, D.L. 598 Clack, D.W. 610, 649, 690 Clark, R.G. 401 Clark, R.G., see Bleaney, B. 401 Claus, H. 478 Claus, H., see Jorgensen, J.D. 475, 478 Claus, H., see Riedling, S. 478 Claus, H., see Schweiss, P. 484 Claus, H., see Yang, S. 478 Clausen, K.N., see Jehan, D.A. 25, 54 Clausen, K.N., see Simpson, J.A. 46, 65 Clem, J.R., see Bulaevskii, L.N. 478 Clementi, E., see Mohanty, A.K. 635 Clerot, F., see Lhomer, C. 596 Clescia, B. 588 Clinton, T.W. 413, 422

Clinton, T.W., see Skanthakumar, S. 413 CNET Group 510 Cochet-Muchy, D. 265 Cochrane, P., see Boggis, J.M. 588 Cochrane, R.W. 392 Cockroft, N.J. 559 Coehoorn, R. 256, 257 Coehoorn, R., see Denissen, C.J.M. 161, 228, 257 Coeurjolly, C., see Clescla, B. 588 Coey, J.M.D. 261 Coey, J.M.D., see Christides, C. 215, 228, 248-250 Coey, J.M.D., see Hu, B.-P. 148, 156, 215, 221, 250, 251 Coey, J.M.D., see Hurley, D.P.F. 261, 263 Coey, J.M.D., see Li, H.-S. 148, 215, 248, 249 Coey, J.M.D., see Otani, Y. 265 Coey, J.M.D., see Qi, Q.-N. 263 Coey, J.M.D., see Sun, H. 265 Coey, J.M.D., see Wang, Xian-zhong 194, 197 Cofied, M.L., see Shin, S.C. 90 Cohen, E. 365 Cohen, E., see Riseberg, L.A. 365 Cohen, E.R. 629 Cohen, M.H. 408 Coldea, M. 167, 168, 181 Coldea, M., see Coldea, R. 167, 168 Coldea, R. 167, 168 Coldea, R., see Coldea, M. 167, 168, 181 Coles, B.R., see Stewart, A.M. 145, 161, 162 Collin, G., see Schweiss, P. 484 Collins, J.R., see Koch, W. 682 Collins, M.F., see Rebelsky, L. 272 Colwell, J.H. 346, 413 Colwell, J.H., see Wright, J.C. 346 Cone, R.L. 343 Cone, R.L., see Lin, G.K. 535 Connor, J.A. 681 Cook, M.I., see Baker, J.M. 444 Cooke, A.H. 346, 404, 405, 413, 417, 420 Cooke, A.H., see Cashion, J.D. 346, 408, 413 Cooper, A.S., see Bucher, E. 305 Cooper, B.R. 14, 30, 61 Cooper, S.L. 477 Cogblin, B. 4, 7, 11 Cordero, F., see Cannelli, G. 477 Cordier, G. 181 Cornehl, H.H., see Heinemann, C. 619, 620, 684, 716 Cornelison, S.G., see O'Shea, M.J. 125 Corruccini, L.R. 408, 413, 421 Corruccini, L.R., see Roser, M.R. 408, 413, 417 Corruccini, L.R., see Xu, J. 413, 417 Corti, M., see Carretta, P. 485

Cory, M.G. 614, 649 Cosmovici, C.B. 673, 674 Cotton, F.A. 690 Courtens, E., see Arrechi, F.T. 530 Courths, R., see Brinkmann, J. 425 Cowan, R.D. 617, 638, 640, 646 Cowan, R.D., see Kahn, L.R. 613, 638, 646 Cowley, R.A., see Bates, S. 13 Cowley, R.A., see Jehan, D.A. 25, 54 Cowley, R.A., see McMorrow, D.F. 46, 63 Cowley, R.A., see Simpson, J.A. 46, 65 Cox, D., see Fillion, G. 413, 428 Cozannet, A. 582 Crabtree, G.W., see Dunlap, B.D. 413 Crabtree, G.W., see Jorgensen, J.D. 475, 478 Crabtree, G.W., see Welp, U. 475 Crawford, M.K., see Phillips, N.E. 490 Cremer, D., see Frenking, G. 682 Cremer, D., see Koch, W. 682 Cromer, D.T., see Waber, J.T. 623 Crow, J.E., see Bulman, J.B. 413 Culberson, J.C. 610, 613, 649, 685, 686, 688, 703 Cullen, J.R., see Callen, E. 137, 138 Cummings, F.W., see Jaynes, E.T. 521 Cundari, T.R. 613, 647, 654, 655, 700, 704, 716, 718 Cunningham, J.E. 14-16 Cunningham, J.E., see Durbin, S.M. 3, 15 Cunningham, J.E., see Flynn, C.P. 47 Cunningham, J.E., see Kwo, J. 3, 14, 16, 20, 39 Cunningham, J.E., see Salamon, M.B. 3, 14, 21, 39, 46, 48 Curl, R.F., see Kroto, H.W. 695 Curl, R.F., see Zhang, Q.L. 696 Custer, J.S., see Polman, A. 599 Czech, E., see Cordier, G. 181 da Costa Jr, N.B., see Andrade, A.V.M. 651, 704, 705, 717 Dabrowski, B., see Jorgensen, J.D. 482 Dabrowski, B., see Zhang, H. 475 Dahl, M. 338 Dahlberg, E.D., see Lottis, D.K. 130 Dallara, J.J., see Richardson, F.S. 318 D'Amico, K.L., see Bohr, J. 30, 54 D'Amico, K.L., see Gibbs, D. 6, 10, 13, 16 Danger, T., see Brede, R. 591 Danielmeyer, H.G. 567 D'Anna, E., see Cosmovici, C.B. 673, 674 Darack, S., see Andres, K. 400 Darshan, B. 174, 175 Dartyge, E., see Baudelet, F. 114 Das, B.N., see Harris, V.G. 119, 140 Das, K.K. 658, 716

738

Das, T.P., see Schmidt, P.G. 317, 324 Datta, S.N. 643 Davey, S.T., see Lauder, R.D.T. 590 Davey, S.T., see Smart, R.G. 592 David, F. 624 David, W.1.F., see Moze, O. 215 David, W.I.F., see Solzi, M. 156, 215, 216, 228, 243-246 Davidova, M.P. 318, 322-324 Davidson, E.R., see Bender, C.F. 610, 685 Davidson, E.R., see Langhoff, S.R. 652, 657 Davidson, M.M., see Cooke, A.H. 413 Davoust, C.E., see Baker, J.M. 444 Day, R.K., see Bingham, D. 319 de Araujo, C.B., see Gomes, A.S.L. 562 de Araujo, C.B., see Rios Leite, J.R. 557 de Boer, F.R. 228, 255 de Boer, F.R., see Andreev, A.V. 154, 202 de Boer, F.R., see Brabers, J.H.V.J. 228, 229 de Boer, F.R., see Haije, W.G. 149, 152, 157, 228, 248 de Boer, F.R., see Verhoef, R. 149, 156, 215, 228, 232, 233, 237, 241, 246, 257 de Boer, F.R., see Yang, F.-M. 232, 233, 248, 249 de Boer, F.R., see Yang, H. 229, 230, 251 de Boer, F.R., see Zhao, Z.G. 135 de Châtel, P.F., see Zhao, Z.G. 135 de Gennes, P.G. 8 de Groot, P. 444 de Groot, P., see Janssen, P. 444 de Jongh, L.J., see Mennenga, G. 346, 413, 420, 458, 468, 469 de Jongh, L.J., see Steiger, J.J.M. 69 De Loach, L.D. 549 de Lozanne, A.L., see Edwards, H.L. 475 de Micheli, M., see Lallier, E. 599 de Micheli, M.P., see Li, M.J. 580, 599 de Mooij, D.B. 148, 156, 209, 215, 222, 228, 232, 234, 237, 241 de Mooij, D.B., see Buschow, K.H.J. 209, 210, 215, 228, 232, 237, 241, 249, 269, 273 de Mooij, D.B., see de Boer, F.R. 228, 255 de Sá, G.F., see Andrade, A.V.M. 651, 704, 705, 717 de Sá, G.F., see Malta, O.L. 600 De Voe, R.G. 531 De Vore, T.C., see Van Zee, R.J. 679 de Vries, M.S., see Johnson, R.D. 699 de Wolf, I., see Janssen, P. 444 De'Bell, K. 422 De'Bell, K., see MacIsaac, A.B. 421 Debray, P., see Hodges, J.A. 475, 485 DeJong, W.A. 635, 707 DeKock, C.W. 686, 687

DeKock, L. 666 DeKock, R.L. 684, 688, 716 Delcroix, P., see Baczewski, C.T. 119 Demers, R.T., see Flynn, C.P. 47 Denissen, C.J.M. 161, 228, 257 DeOliveira, A.C., see Bleaney, B. 372, 373 Deportes, J. 145, 158, 159 Deportes, J., see Yang, Y.C. 233 Deppish, B., see Lohmuller, G. 304 Deryagin, A.V. 270 Desclaux, J.P. 612, 615-617, 623, 634, 650 Desclaux, J.P., see Freeman, A.J. 322 Desclaux, J.P., see Pyykkö, P. 610, 612, 617, 619, 625, 684 Desmoulins, C., see Tomey, E. 237, 261 Desurvire, E. 511, 537, 557, 580, 587, 588 Desurvire, E., see Giles, C.R. 587 Deutschbein, O.K. 510, 575 Deutschbein, O.K., see Auzel, F. 557 Deutscher, G. 478 Dewar, M.J.S. 651, 699, 704 Dexpert-Ghys, J. 538, 539, 549 Dexpert-Ghys, J., see Auzel, F. 570, 572 Dexpert-Ghys, J., see Santa-Cruz, P.A. 578, 599 Dexter, D.L. 551, 553, 558 Dexter, D.L., see Fowler, W.B. 542 Dexter, D.L., see Miyakawa, T. 544, 545, 548, 552 Dexter, D.L., see Stavola, M. 558 Dhar, S.K., see Malik, S.K. 174, 175 Di Bartolo, B. 510, 564 Di Salvo, F.J., see Kwo, J. 3, 14, 20-22, 30, 39, 47 DiBella, S. 684, 688, 716 Dick, B.G. 317 Dickson, D.P.E., see O'Grady, K. 127 Dieke, R.H. 512, 524, 526 Diener, M.D., see Guo, T. 696 Dietz, R.E., see Johnson, L.F. 549 Digiovanni, D.J., see Zyskind, J.L. 600 Digonnet, M.J.F. 511, 537, 580, 588 Dillon Jr, J.F., see van Dover, R.B. 94 Ding, J. 209, 218, 228, 265 Ding, Y.-F., see Lin, C. 209, 271, 272, 278 Ding, Y.-F., see Yang, Y.-C. 216, 261 D'Innocenzo, A., see Cosmovici, C.B. 673, 674 D'Iorio, M. 365 Dirac, P.A.M. 630, 640 Dirken, M.W. 157, 215, 228, 241, 243 Dirkmaat, A.J. 459, 469-471 Discherl, G., see Cosmovici, C.B. 673, 674 Dixit, S.N., see De Loach, L.D. 549 Dixon, R.N. 646 Djeu, N., see Scott, B.P. 591

Dmowski, W., see Egami, T. 94 Dobosh, P.A., see Pople, J.A. 649 Dodson, B.W. 26 Dohm, V. 310, 326 Dolg, M. 613, 618-620, 625, 628, 629, 635, 640, 643, 647, 648, 651-670, 672-683, 686-688, 692-695, 713, 716 Dolg, M., see Andrae, D. 647 Dolg, M., see Bergner, A. 647 Dolg, M., see Heinemann, C. 619, 620, 684, 716 Dolg, M., see Kaupp, M. 690, 716 Dolg, M., see Küchle, W. 613, 618, 619, 625, 640, 647, 670 Dolg, M., see Schwerdtfeger, P. 682, 716 Dolg, M., see Seth, M. 626, 627, 647 Dommann, M., see Hess, G. 459, 466, 467 Dong, N. 705, 717 Dong, S.-T., see Yang, Y.-C. 261, 263 Dong, Z., see Hu, J. 218 Doniach, S. 185 Dooglav, A.V. 484, 485 Dooglav, A.V., see Bakharev, O.N. 318, 323, 472, 479, 481-483, 486-491 Dooglav, A.V., see Egorov, A.V. 479, 483-485 Dooglav, A.V., see Ishigaki, T. 318, 323 Dooglav, A.V., see Teplov, M.A. 479, 487, 489 Doran, J.C., see Landau, D.P. 413 Dorenbos, P., see Andriessen, J. 714, 716 Dorenbos, P., see Visser, R. 710, 712, 713, 716 Dorfler, W. 338 Douay, M., see Carette, P. 666, 667 Douglas, M. 637, 641 Dowben, P.A., see Li, D.Q. 35 Downey, J.W., see Veal, B.W. 475, 478, 488 Downey, J.W., see Welp, U. 475 Downey, J.W., see Yang, S. 478 Dravid, V.P., see Zhang, H. 475 Drexhage, D.C., see Yeh, D.C. 593 Drexhage, M.G., see Quimby, R.S. 593 Drulis, H., see Andreev, A.V. 269, 274, 275 Drulis, H., see Berezyuk, D.A. 147, 233, 234, 237, 240, 242, 243 Drulis, H., see Suski, W. 157, 234, 268, 273, 279, 280 Drulis, H., see Vagizov, F.G. 154, 188, 189, 194, 195, 200-202, 268, 283-285 Drulis, M. 181, 183 Drzazga, Z. 148, 169, 174-176 Du, R.-R. 17, 19, 66 Du, R.-R., see Beach, R.S. 57 Du, R.-R., see Borchers, J.A. 11, 24, 30, 42, 46, 55, 57, 58 Du, R.-R., see Erwin, R.W. 40, 41, 44, 46, 48, 52, 54

Du, R.-R., see Flynn, C.P. 47 Du, R.-R., see Huang, J.-C. 17, 19 Du, R.-R., see Rhyne, J.J. 46, 48, 49, 51, 52 Du, R.-R., see Salamon, M.B. 3, 48 Du, R.-R., see Tanaka, Y. 25, 30, 31 Du Tremolet de Lacheisserie, E., see Morin, P. 359 Dufour, C., see Cherifi, K. 109-111 Duglav, A.V., see Al'tshuler, S.A. 363, 365, 386 Dulick, M. 650, 660-662, 666, 667, 669-674, 676 Dulick, M., see Linton, C. 667, 668, 672-674 Dunlap, B.D. 413 Dunlap, B.I. 641, 696 Dunlap, B.I., see Häberlen, O.D. 716 Dunlap, B.I., see Rösch, N. 629, 641, 696, 697, 716 Dunlop, J.B., see Bingham, D. 319 Dunlop, J.B., see Cadogan, J.M. 203 Dupas, C., see Beauvillain, P. 424 Dura, J.A., see Cunningham, J.E. 14 Dura, J.A., see Flynn, C.P. 47 Dura, J.A., see Mayer, J. 16 Dura, J.A., see Reimer, P.M. 16 Durand, J., see Baczewski, C.T. 119 Durand, P. 646 Durand, P., see Barthelat, J.C. 640, 646 Durand, P., see Chang, C. 638 Durbin, S.M. 3, 15 Dvornikova, A.E., see Sokolov, V.I. 459, 466-468 Dvornikova, A.E., see Vasil'ev, A.V. 459, 466, 467 Dyall, K.G. 612, 613, 623, 624, 634-636, 655

Eaglesham, D.J., see Adler, D.L. 598 Eberly, J.H., see Allen, H. 521, 523-525 Ebert, H., see Schütz, G. 140 Eckert, J., see Schlachetzki, A. 405 Edagawa, E. 587 Edagawa, N., see Wakabayashi, H. 587 Edelstein, N., see Morss, L.R. 305 Edelstein, N.M., see David, F. 624 Edelstein, N.M., see Loong, C.-K. 318, 319, 321, 322 Edelstein, N.M., see Thornton, G. 641 Eden, D.D., see Chivian, J.S. 511 Eden, J.G., see Funk, D.S. 599 Edmonds, D.T., see Cooke, A.H. 404, 405, 413, 417 Edwards, H.L. 475 Effantin, C., see Bernard, A. 661, 673 Egami, T. 94 Egami, T., see Yan, X. 119

Egorov, A.V. 363, 366-368, 370, 373, 376, 377, 400, 479, 483-485 Egorov, A.V., see Bakharev, O.N. 318, 323, 472, 479, 481-483, 486-491 Egorov, A.V., see Dooglav, A.V. 484, 485 Egorov, A.V., see Lütgemeier, H. 479 Egorov, A.V., see Teplov, M.A. 479, 487, 489 Egorov, A.V., see Volodin, A.G. 386 Eick, H.A., see Hariharan, A.V. 687 Eijk, C.W.E., see Visser, R. 710, 712, 713, 716 Einstein, A. 629 Elam, W.T., see Harris, V.G. 119, 120, 140 Elbicki, J., see Sinha, V.K. 215, 218 Elbicki, J.M., see Cheng, S.F. 218 Eliav, E. 613, 627, 635, 651, 652, 669 Ellingsen, O.S. 346, 413, 417 Elliott, R.J. 4, 6, 7, 10, 16, 319, 329 Elliott, R.J., see Harley, R.T. 458, 467 Ellis, D.E. 610, 685 Ellis, D.E., see Guo, C. 610 Ellis, D.E., see Rosén, A. 641, 700 Ellman, B., see Reich, D.H. 458, 469-471 Ellman, B., see Rosenbaum, T.F. 458 Elmaleh, D. 413, 420 Emel'chenko, G.A., see Bredikhin, S.I. 477 Emerson, J.P. 490 Emerson, J.P., see Phillips, N.E. 490, 491 Emery, V.J. 479 Emery, V.J., see Kivelson, S.A. 479 Enderle, M. 318, 319 Endl, G., see Ertl, L. 90, 106, 108 Engelman, R. 545 England, N.J., see Cooke, A.H. 413 Enikeev, K.M., see Krjukov, E.V. 479, 488, 489 Ennen, H. 594, 595 Ennen, H., see Kaufman, U. 595 Erath, E.H. 323 Erb, A., see Claus, H. 478 Erb, A., see Riedling, S. 478 Erb, A., see Schweiss, P. 484 Erdmann, K., see Sinnemann, Th. 209, 215, 228, 241 Erdos, P. 314 Eremin, M.V. 312, 314, 325, 369, 371, 372, 490 Eremin, M.V., see Bakharev, O.N. 490 Eremin, M.V., see Egorov, A.V. 373 Eremin, M.V., see Teplov, M.A. 479 Erickson, M.G., see Kaledin, L.A. 666 Ermler, W.C. 612, 613, 646 Ermler, W.C., see Chang, A.H.H. 648, 691, 697, 698, 717 Ermler, W.C., see Christiansen, P.A. 612, 646 Ermler, W.C., see Hurley, M.M. 646 Ermler, W.C., see LaJohn, L.A. 646

Ermler, W.C., see Lee, Y.S. 647 Ermler, W.C., see Ross, R.B. 613, 646, 654, 655 Ermolenko, A.S. 154, 155, 207, 209, 233, 234, 237, 249, 250 Ernst, R.D., see Marks, T.J. 689 Ertl, L. 90, 106, 108 Erwin, R.W. 40, 41, 44, 46, 48, 52, 54 Erwin, R.W., see Beach, R.S. 21, 22, 45, 46, 59, 62 Erwin, R.W., see Borchers, J.A. 11, 24, 30, 42, 46, 55, 57, 58 Erwin, R.W., see Everitt, B.A. 10, 14, 25, 65 Erwin, R.W., see Flynn, C.P. 47, 66 Erwin, R.W., see Rhyne, J.J. 46, 48, 49, 51, 52 Erwin, R.W., see Salamon, M.B. 3, 14, 21, 39, 46, 48, 52, 70 Erwin, R.W., see Tsui, F. 65, 66, 68 Erwin, R.W., see Yang, K.N. 413 Esaki, L., see Chang, L.L. -15 Esser, M. 613, 635, 648 Esterowitz, L., see Kintz, G.J. 557 Estrele, P., see Gonçalves, A.P. 268, 269, 272, 286 Etedgi, H., see Gal, J. 174, 176 Etourneau, J., see Berlureau, T. 157, 267, 268, 272, 277, 278, 281 Etourneau, J., see Matar, S.F. 270, 286 Etourneau, J., see Wang, Xian-zhong 194, 197 Evenson, W.E. 9 Everitt, B.A. 10, 14, 25, 65 Ewig, C.S., see Datta, S.N. 643 Faegri, K., see Almloef, J. 638 Faegri, K., see Dyall, K.G. 635 Faegri, K., see Visscher, L. 613, 635, 708 Fagan, A., see Tomey, E. 237, 261 Fahrle, M. 35 Falicov, L.M. 20, 32, 35, 47 Falkovskaya, L.D., see Ivanov, M.A. 459, 460 Fang, Y., see Veal, B.W. 475, 478, 488 Fanning, M.O. 649 Farrow, R.F.C. 21 Fatuzzo, E. 128, 140 Faucher, M. 314, 317, 324 Faucher, M., see Garcia, D. 312, 314, 322 Faut, J., see Allenspach, P. 479 Favennec, P.N. 594, 597 Favennec, P.N., see Rochaix, C. 594 Favennec, P.N., see Rolland, A. 595, 596 Favorskii, I.A. 418 Fedii, A.A., see Antipin, A.A. 382, 384, 385, 390, 392, 393 Fedorov, A.A., see Ovsyankin, V.V. 557 Feger, A., see Anders, A.G. 408

Felcher, G.P., see Broach, R.W. 302, 303, 370, 448 Feld, M.S., see MacGillivray, J.C. 525, 529 Feld, M.S., see Skribanowitz, N. 525, 527, 535 Feldman, L.C., see Kwo, J. 3, 14, 16, 20, 39 Feller, G., see Volodin, A.G. 386 Felner, I. 148, 163, 165, 167-169, 174, 175, 178, 181, 182, 185–188, 190, 191, 194–201 Felner, I., see Nowik, I. 148, 154 Felner, I., see Wortmann, G. 413 Felsteiner, J. 408 Felsteiner, J., see Misra, S.K. 408, 420 Felten, R., see Drulis, M. 181, 183 Fényes, 1. 642 Feofilov, P.P., see Ovsyankin, V.V. 511, 556, 557 Fermon, C., see Roinel, Y. 386 Fernando, A.S. 215, 228, 232, 258 Ferrand, B., see Chartier, I. 600 Ferrand, B., see Pelenc, D. 600 Ferrand, B., see Sheperd, D.P. 600 Ferrante, R.F., see Van Zee, R.J. 666, 667 Ferre, J., see Pommier, J. 404 Ferreira, J.M., see Yang, K.N. 413 Ferretti, M., see Cannelli, G. 477 Fert, A., see Perera, P. 106 Feuss, H. 304 Feyrier, H., see Marcerou, J.F. 588 Field, R.W. 614, 627, 628, 647, 650, 660, 661, 668, 669, 672, 673 Field, R.W., see Dulick, M. 676 Field, R.W., see Linton, C. 667, 668, 672-674 Field, R.W., see McDonald, S.A. 651, 673, 675 Field, S.J., see Chartier, I. 600 Fietz, W.H., see Metzger, J. 477 Figiel, H., see Baran, A. 267, 268, 271, 273 Filippi, J. 413 Fillion, G. 413, 428 Finn, C.B.P., see Cooke, A.H. 404, 405, 413, 417 Fischer, P., see Attenkofer, K. 114, 115 Fischer, P., see Guillaume, M. 473 Fischer, P., see Kockelmann, W. 154, 185-188 Fischer, P., see Roessli, B. 413 Fischer, P., see Schäfer, W. 185 Fischer, P., see Schütz, G. 140 Fischer, R.D., see Marks, T.J. 689 Fish, G.E. 373 Fishel, N.A., see Hariharan, A.V. 687 Fisher, R.A., see Emerson, J.P. 490 Fisher, R.A., see Lee, W.C. 487 Fisher, R.A., see Phillips, N.E. 490, 491 Fishman, A.Ya., see Ivanov, M.A. 459, 460 Fishman, S., see Rohrer, H. 468 Fisk, Z., see Hundley, M.F. 413 Fisk, Z., see Skanthakumar, S. 413

Fisk, Z., see Vaknin, D. 479 Fitzpatrick, N.J., see Fanning, M.O. 649 Fitzpatrick, W.J., see Mehran, F. 387, 391, 398 Fitzwater, D.R. 301 Flad, H.-J., see Dolg, M. 620, 629, 648, 651, 653, 654, 668, 673-676, 716 Flanders, P.J., see Egami, T. 94 Fleig, T. 638 Fleming, R.M., see Kwo, J. 21, 22, 30 Fleming, R.M., see Majkrzak, C.F. 46 Fleshler, S., see Welp, U. 475 Fleuret, J., see Cozannet, A. 582 Florian, R. 527, 532 Florio, J.V. 145 Flynn, C.P. 15, 16, 19, 47, 66 Flynn, C.P., see Beach, R.S. 21, 22, 24, 25, 30, 45, 46, 57, 59, 62 Flynn, C.P., see Borchers, J.A. 11, 24, 30, 42, 46, 55, 57, 58 Flynn, C.P., see Cunningham, J.E. 14–16 Flynn, C.P., see Du, R.-R. 17, 19, 66 Flynn, C.P., see Durbin, S.M. 3, 15 Flynn, C.P., see Erwin, R.W. 40, 41, 44, 46, 48, 52, 54 Flynn, C.P., see Everitt, B.A. 10, 14, 25, 65 Flynn, C.P., see Huang, J.-C. 17, 19 Flynn, C.P., see Majkrzak, C.F. 46 Flynn, C.P., see Mayer, J. 16 Flynn, C.P., see Reimer, P.M. 16 Flynn, C.P., see Rhyne, J.J. 46, 48, 49, 51, 52 Flynn, C.P., see Salamon, M.B. 3, 14, 21, 39, 46, 48, 52, 70 Flynn, C.P., see Tanaka, Y. 25, 30, 31 Flynn, C.P., see Tsui, F. 18, 21, 22, 26, 35, 36, 65, 66, 68 Flynn, C.P., see Yang, M.-H. 3, 15 Fock, V. 632, 634 Folcik, L., see Naydyuk, Yu.G. 151, 181, 183, 189 Folcik, L., see Suski, W. 181, 184, 185, 268, 272, 282, 283 Foldy, L.L. 636 Folinsbee, J.T. 346, 428 Folkins, J.J. 458, 468, 469 Folkins, J.J., see Griffin, J.A. 458 Folle, H.R. 400 Folweiler, R.J., see Griffin, J.A. 425 Foner, S., see Bulman, J.B. 413 Fong, F.K. 545, 546, 548 Fonger, W.H., see Struck, C.W. 545 Fontaine, A., see Baudelet, F. 114 Fontaine, A., see Tolentino, H. 486 Fontaine, D. 473 Förster, T. 550

Forsyth, J.B., see Bleaney, B. 408 Forsyth, J.B., see Brown, P.J. 413, 416 Fournes, L., see Berlureau, T. 157, 267, 268, 272, 277, 278, 281 Fournier, G., see Roinel, Y. 386 Fournier, J.-M. 150 Fowler, W.B. 542 Fox, T., see Kotzian, M. 702, 717 Fragalà, I.L., see DiBella, S. 684, 688, 716 Fragalà, I.L., see Streitwieser, A. 610, 689, 691 France, P.W., see Brierley, M.C. 588 Franke, R., see Kutzelnigg, W. 636 Frankevich, D.P., see Kuz'ma, Yu.B. 161 Franse, J.J.M., see Kim-Ngan, N.H. 168 Franse, J.J.M., see Verhoef, R. 135 Franz, J., see Claus, H. 478 Fredo, S., see Gal, J. 150, 154, 163, 165, 176-178, 181, 182, 185, 201 Fredo, S., see Halevy, I. 186-189, 202 Freeman, A.J. 7, 9, 322, 324 Freeman, A.J., see Rath, J. 258 Fremy, M.A., see Le Roy, J. 263 Frenking, G. 682 Frenking, G., see Jørgensen, C.K. 682 Frenking, G., see Koch, W. 682 Freund, L.B. 26 Frey, E. 425 Fricke, B., see Desclaux, J.P. 623 Friedberg, R. 530 Friedberg, S.A., see Bellesis, G.H. 413 Friedberg, S.A., see Petasis, D.T. 346, 413, 428 Friedberg, S.A., see Simizu, S. 413, 418, 458, 469 Friedman, Z., see Felsteiner, J. 408 Frikkee, E., see Steiger, J.J.M. 69 Froese Fischer, C. 634, 655 Froese Fischer, C., see Cai, Z. 613, 651, 652 Froese Fischer, C., see Hibbert, A. 634 Frowein, R. 417, 424, 425 Fruchart, D., see Elmaleh, D. 413, 420 Fruchart, D., see Garcia, L.M. 237-239, 246, 247, 252 Fruchart, D., see Luis, F. 237, 238, 252 Fruchart, D., see Tomey, E. 237, 261 Fruchart, R., see Luis, F. 237, 238, 252 Fu. H. 120 Fu, H., see Wu, T.-H. 134-136 Fuentealba, P. 647 Fuerst, C.D., see Capehart, T.W. 234 Fujii, H., see Akayama, M. 215 Fujii, H., see Sun, H. 258, 259 Fujii, S., see Asano, S. 259 Fujii, S., see Ishida, S. 258 Fujimura, T., see Goto, T. 351, 354, 357, 358

Fujiwara, H. 148, 169, 174, 175 Fujiwara, H., see Kamimori, T. 162, 174, 198, 200 Fujiwara, H., see Liu, W.L. 198 Fukamichi, K., see Malozemoff, A.P. 259 Fukasaku, Y., see Miyajima, Y. 590 Fulde, P. 622 Fulde, P., see Dohm, V. 310, 326 Fulde, P., see Dolg, M. 629, 647, 648, 654, 655, 692-694, 716 Fulde, P., see Neumann, C.-S. 692 Fulde, P., see Seth, M. 626, 627, 647 Fulde, P., see Thalmeier, P. 431 Funahashi, S., see Sun, H. 258, 259 Funk, D.S. 599 Fure, J., see Chai, Y. 696, 699 Furrer, A. 318, 323, 422, 475 Furrer, A., see Allenspach, P. 318, 323, 479 Furrer, A., see Guillaume, M. 318, 323, 473 Furrer, A., see Mesot, J. 323, 475, 478 Furrer, A., see Podlesnyak, A. 318 Furrer, A., see Roessli, B. 413 Furubayashi, T., see Ishimoto, H. 400 Gabbe, D., see Griffin, J.A. 458 Gabelnick, S.D. 670, 671, 673, 684 Gain Project 589, 590 Gajewski, D., see Allenspach, P. 413, 422 Gal, J. 150, 154, 163, 165, 174, 176-178, 181, 182, 185, 201 Gal, J., see Halevy, I. 186-189, 202 Gal, J., see Kockelmann, W. 154, 185-188 Gal, J., see Schäfer, W. 174, 176-178, 185 Galamushka, L.T., see Kuz'ma, Yu.B. 146, 154 Galtier, P., see Benyattou, T. 596 Galtier, P., see Charasse, M.N. 594 Galuza, A.I., see Beznosov, A.B. 150, 273 Gambino, R.J., see Cadieu, F.J. 215 Gao, J.-L., see Yang, Y.-C. 218, 219, 222, 243 Garcia, D. 312, 314, 322 Garcia, D., see Faucher, M. 314, 317, 324 Garcia, L.M. 215, 237-239, 246, 247, 252 Garcia, L.M., see Luis, F. 237, 238, 252 Garrett, C.G.B., see Kaiser, W. 510 Garrett, J.B., see Rebelsky, L. 272 Garrison, K., see Li, D.Q. 35 Gauneau, M., see Favennec, P.N. 594, 597 Gauneau, M., see Lambert, B. 596 Gauneau, M., see Lhomer, C. 596 Gauneau, M., see Rolland, A. 595, 596 Gaunt, J.A. 632 Gauss, J., see Koch, W. 682 Gautier, C., see Auzel, F. 570, 572 Gavigan, J.P., see Hu, B.-P. 156, 215

Gavigan, J.P., see Li, H.-S. 215, 248 Gayen, S., see Ross, R.B. 613, 646, 654, 655 Ge, S.-L. 209, 215 Ge, S.-L., see Yang, Y.-C. 237, 261 Gebhard, U., see Claus, H. 478 Gehring, G.A. 299, 346, 413, 417, 419, 458, 459, 466 Gehring, K.A., see Gehring, G.A. 299, 413 Geibel, C. 154, 183 Geibel, C., see Krimmel, A. 150, 152, 154, 162, 181, 183, 184, 189 Geibel, C., see Lunkenheimer, P. 185 Geibel, C., see Suski, W. 185, 268, 272, 282, 283 Genack, A.Z. 531 Genet, M., see Brandel, V. 577 Geng, M.M. 237 Geng, M.M., see Ma, R.H. 209, 228, 247 Genoud, J.-Y., see Sanchez, D. 490 Gérard, I. 715, 716 German, N.V., see Koterlin, M.D. 167, 174, 181, 182 Giapintzakis, J., see Cooper, S.L. 477 Gibbs, D. 6, 10, 13, 16 Gibbs, D., see Bohr, J. 30, 54 Gibbs, D., see Isaacs, E.D. 6, 10, 13, 16 Gibbs, D., see Kwo, J. 21, 22, 30 Gibbs, D., see Majkrzak, C.F. 3, 46, 48, 54, 65 Gibbs, D., see Tanaka, Y. 25, 30, 31 Gigli, G., see Guido, M. 651 Gignoux, D., see Garcia, L.M. 237-239, 246, 247, 252 Gignoux, D., see Luis, F. 237, 238, 252 Gignoux, D., see Tomey, E. 237 Giles, C.R. 587 Giles, C.R., see Desurvire, E. 587 Giles, R.C. 132 Giles, R.C., see Mansuripur, M. 132 Gilfrich, J., see Wang, F.C. 145 Ginsberg, D.M., see Cooper, S.L. 477 Giordano, N., see Fillion, G. 413, 428 Giordano, N., see Stryjewski, E. 418 Giorgi, A.L., see Geibel, C. 154, 183 Girichev, G.V., see Krasnov, K.S. 686 Giricheva, N.I., see Krasnov, K.S. 686 Givord, D., see Deportes, J. 145, 158, 159 Gladyshevsky, E.I. 146-148, 154, 156, 206 Glas, F., see Santa-Cruz, P.A. 578, 599 Glasman, L.I., see Bulaevskii, L.N. 478 Glass, R., see Hibbert, A. 634 Gleichmann, M.M. 637 Glenn, W.H., see Ball, G.A. 600 Glynn, T.J. 365, 458, 467 Gobel, H., see Will, G. 419 Goddard III, W.A., see Rappé, A.K. 646

Godefroid, M.R., see Froese Fischer, C. 634 Godinho, M., see Gonçalves, A.P. 268, 269, 272, 286 Godinho, M., see Paixão, J.A. 177, 178, 202, 286 Goldman, A.I., see Kwo, J. 21, 22, 30 Goldman, A.I., see Majkrzak, C.F. 46 Goldman, M., see Abragam, A. 401, 403 Goldman, M., see Chapellier, M. 401 Goldner, P., see Auzel, F. 559, 593 Goldner, P., see Pellé, F. 559 Goldschmidt, Y.Y. 36, 70 Golka, E., see Stoll, H. 641, 659, 667, 680 Gombás, P. 642, 645 Gomes, A.S.L. 562 Gonçalves, A.P. 148, 169, 268, 269, 272, 286 Gonçalves, A.P., see Paixão, J.A. 177, 178, 202, 286 Gong, W. 261 Goodman, G.L., see Ellis, D.E. 610, 685 Goodman, G.L., see Loong, C.-K. 319, 321 Goodman, G.L., see Ruščić, B. 610, 641, 685, 686 Goodwin, T.J., see Clinton, T.W. 422 Goodwin, T.J., see Rosov, N. 413 Gordon, J.E., see Phillips, N.E. 490, 491 Gordon, W. 640 Goremychkin, E.A., see Osborn, R. 484 Gorman, G., see Beyers, R. 474, 475 Gościańska, I., see Lunkenheimer, P. 185 Gotkis, I. 628, 677 Goto, M., see Kamimori, T. 162, 174, 198, 200 Goto, M., see Liu, W.L. 198 Goto, T. 351, 354, 357, 358 Goto, T., see Andreev, A.V. 247, 267, 275, 276, 284-286 Gottwick, U., see Rauchschwalbe, U. 178, 181-183, 195 Gouedard, C. 538, 539 Gourieux, T., see Tolentino, H. 486 Gozen, T., see Haruna, M. 599 Grabmaier, B.C., see Blasse, G. 599 Graf, T. 472, 473, 483, 490 Graf, T., see Sanchez, D. 490 Graham Jr, C.D., see Egami, T. 94 Graham, J.T. 459 Grahl, M. 405 Gramlich, V., see Lohmuller, G. 304 Grandpierre, G., see Lambert, B. 596 Grant, I.P. 612, 634 Grant, I.P., see Dyall, K.G. 612, 623, 624, 634, 655 Grant, I.P., see Rose, S.J. 617, 643 Grant, W.J.C. 555 Grattepain, C., see Charasse, M.N. 594

Gravereau, P., see Berlureau, T. 157, 268, 272, 277, 278, 281 Graves, D.T., see Myers, C.E. 687 Greaves, S.J., see O'Grady, K. 126-128 Greco, A. 689 Gregg, J.F., see Bleaney, B. 318, 322, 351, 363, 364, 366, 367, 372, 387, 401, 416, 429 Greis, O., see Petzel, T. 687 Grelland, H.H., see Almloef, J. 638 Grevtsev, V.A., see Al'tshuler, S.A. 444 Grevtsev, V.A., see Aukhadeev, F.L. 431 Grezes-Besset, C., see Lallier, E. 599 Grieb, B., see Neiva, A.C. 146, 147 Grier, B.H., see Gibbs, D. 13 Griffin, D.C., see Cowan, R.D. 617, 638, 640, 646 Griffin, J.A. 404, 423, 425, 458 Griffin, J.A., see Brierley, S.K. 468 Griffin, J.A., see Folkins, J.J. 458, 468, 469 Griffin, J.A., see Youngblood, R.W. 468 Griffiths, J.S. 342 Grimm, H., see Kwo, J. 21, 22, 30 Grimm, H., see Majkrzak, C.F. 46 Grimsditch, M., see Welp, U. 475 Grin, Yu.N., see Weitzer, F. 146, 202, 203, 205, 206 Grodkiewicz, W.H., see Singh, S. 538 Grodkiewicz, W.H., see Van der Ziel, J.P. 557 Grohmann, I. 319 Gronsky, R., see Falicov, L.M. 20, 32, 35, 47 Gropen, O. 646 Gropen, O., see Marian, C.M. 670 Gropen, O., see Visscher, L. 613, 635, 708 Gross, M. 524 Gross, M., see Carlson, N.W. 536 Grössinger, R. 228, 246 Grössinger, R., see Christides, C. 237, 273 Grössinger, R., see Katter, M. 265 Grubb, S.G. 592 Grube, K., see Metzger, J. 477 Grübel, G., see Gibbs, D. 13 Grünberg, P. 39 Grutz, A., see Braunisch, W. 478 Gu, D.M., see Yang, Y.-C. 215, 243, 245 Guan, W.Y. 413 Gubbens, P.C.M. 209, 215, 228, 232, 233, 253, 257, 275 Gubser, D.U., see Folkins, J.J. 458, 468, 469 Güdel, H.U., see Oetliker, U. 561 Guégan, H., see Barrière, A.S. 600 Gueramian, M. 154, 156, 242, 243, 246, 268, 273 Guertin, R.P., see Bulman, J.B. 413 Guggenheim, H.G. 591 Guggenheim, H.J., see Ahlers, G. 424, 425 Guggenheim, H.J., see Als-Nielsen, J. 302, 413

Guggenheim, H.J., see Brinkmann, J. 425 Guggenheim, H.J., see Bucher, E. 305 Guggenheim, H.J., see Holmes, L.M. 346, 413, 415, 420 Guggenheim, H.J., see Johnson, L.F. 549 Guggenheim, H.J., see Reich, D.H. 458, 469 Guibert, M., see Clescla, B. 588 Guibert, M., see Ronarc'h, D. 537, 588, 589 Guido, M. 651 Guillaume, M. 318, 323, 473 Guillaume, M., see Allenspach, P. 479 Guillaume, M., see Roessli, B. 413 Guillaumont, R., see David, F. 624 Guillot, G., see Benyattou, T. 596 Guimpel, J., see Welp, U. 475 Guo, C. 610 Guo, T. 696 Guo, T., see Chai, Y. 696, 699 Gupta, R.P., see Liu, S.H. 9 Gur, T.M., see Beyers, R. 474, 475 Gurvich, L.V., see Kulikov, A.N. 667 Gutenkundst, G., see Mayer, J. 16 Guttmann, A.J. 413 Guy, S., see Joubert, M.F. 511 Gyorgy, E.M., see Hellman, F. 119, 120 Gyorgy, E.M., see Kwo, J. 3, 14, 16, 20, 39, 47 Gyorgy, E.M., see van Dover, R.B. 94 Gyorgy, E.M., see Vettier, C. 46 Haas, Y. 538, 539 Häberlen, O.D. 638, 641, 696, 716 Häberlen, O.D., see Rösch, N. 629, 638, 641, 696, 697, 716 Habitz, P., see Chang, T.-C. 643, 644 Habitz, P., see Hafner, P. 622 Habu, K., see Sato, N. 90, 94, 134 Habu, K., see Yamauchi, K. 90 Hadjiev, V.G. 476, 489 Hadjiev, V.G., see Iliev, M. 475 Hadjipanayis, G.C., see Gong, W. 261 Hadjipanayis, G.C., see Singleton, E.W. 263.264 Hadjipanayis, G.C., see Strzeszewski, J. 263, 265 Hadjipanayis, G.C., see Wang, Y.Z. 228, 263, 264 Hadjipanayis, G.C., see Yellon, B.W. 258 Hadjipanayis, G.C., see Zhao, Z.R. 265 Hafner, P. 622, 643, 645, 648 Hagan, L., see Martin, W.C. 609, 612, 619, 652-654, 671, 682, 701 Haghighi, M.S. 695 Hagmann, N., see Jehan, D.A. 25, 54 Haije, W.G. 149, 152, 157, 228, 248 Hajjar, R.A., see Wu, T.-H. 134-136 Haken, H. 517 Halbritter, J. 478

Halevy, I. 186-189, 202 Halperin, B.I., see Aharony, A. 424 Ham, F.S. 330, 343 Hamada, N., see Kobayashi, H. 610, 700, 701 Hamann, D.R. 646 Hamann, D.R., see Bachelet, G.B. 646, 699 Hammann, J. 413 Hammann, J., see Radhakrishna, P. 304, 413, 419 Hammonds, J.P., see Loong, C.-K. 319, 321, 322 Hamon, L., see Clescla, B. 588 Han, D., see Tsui, F. 18, 35 Hanna, D.C., see Carter, J.N. 590 Hanna, D.C., see Chartier, I. 600 Hanna, D.C., see Lauder, R.D.T. 590 Hanna, D.C., see Pelenc, D. 600 Hanna, D.C., see Percival, R.M. 590 Hanna, D.C., see Sheperd, D.P. 600 Hanna, D.C., see Smart, R.G. 592 Hansen, P.C., see Bleaney, B. 318, 322, 366, 367 Hansen, P.C., see Brown, P.J. 413, 416 Hansen, P.E. 443 Hansen, P.E., see Beauvillain, P. 413 Hansen, P.E., see Magarino, J. 444 Hansen, P.E., see Nevald, R. 443 Hardy, R.J., see Kirby, R.D. 83, 105, 125, 130, 131 Hardy, W.N., see Schleger, P. 486 Hariharan, A.V. 687 Harley, R.T. 351, 354, 360, 365, 409, 458, 467 Harley, R.T., see Bleaney, B. 363, 366 Harley, R.T., see Elliott, R.J. 319, 329 Harley, R.T., see Glynn, T.J. 365, 458, 467 Haroche, S., see Carlson, N.W. 536 Haroche, S., see Gross, M. 524 Harris, T.D., see Schubert, E.F. 600 Harris, V.G. 119, 120, 140 Harrison, J.P. 346, 428 Harrison, J.P., see Folinsbee, J.T. 346, 428 Harrison, J.P., see Taylor, D.R. 428 Harrison, W.A. 260, 261 Harshman, D.R., see Gibbs, D. 6, 10, 13, 16 Hartmann, S.R., see Friedberg, R. 530 Hartmann, S.R., see Kurnit, N.A. 526, 531 Hartmann, S.R., see Tse, D. 487 Hartree, D.R. 632, 634 Haruna, M. 599 Hasegawa, R. 116 Haslett, T.L., see Kirkwood, A.D. 681 Hastie, J.W. 687 Hastings, J.B., see Isaacs, E.D. 6, 10, 13, 16 Hathaway, K.B., see Falicov, L.M. 20, 32, 35, 47 Hattori, K. 599 Hattori, K., see Kitagawa, T. 599, 600 Haufler, R.E., see Chai, Y. 696, 699

Haufler, R.E., see Guo, T. 696 Hauge, R.H., see Hastie, J.W. 687 Häußermann, U., see Andrae, D. 647 Havela, L., see Sechovsky, V. 148, 150, 272, 281 Havriliak, S., see Stanton, R.E. 635 Hawkes, J.F.B. 343 Hay, P.J. 639, 646, 661, 665, 684, 688, 699, 700 Hay, P.J., see Kahn, L.R. 613, 638, 646 Hay, P.J., see Martin, R.L. 618, 638 Hay, P.J., see Wadt, W.R. 639, 646 Hayden, S.M., see Leask, M.J.M. 415, 416 Hayes, E.F. 684, 688 Hayes, W., see Elliott, R.J. 319, 329 Hayes, W., see Glynn, T.J. 365 Hayes, W., see Harley, R.T. 365, 458, 467 Hazi, A.U. 642 Hazi, A.U., see Weeks, J.D. 646 He, C., see Huang, L. 705 He, Q., see Lallier, E. 599 Healy, E.F., see Dewar, M.J.S. 651, 699, 704 Heath, J.R., see Kroto, H.W. 695 Heath, J.R., see Zhang, Q.L. 696 Heaven, M.C., see Kaledin, L.A. 665, 666, 668, 669 Hebert, T. 564, 591 Hebral, B., see Filippi, J. 413 Hegarty, D., see Visser, O. 631 Hegde, H. 146, 160, 161 Hegde, H., see Cadieu, F.J. 215, 264 Hegde, H., see Kamprath, N. 264, 266 Hegde, H., see Navarathna, A. 160 Heger, G., see Schweiss, P. 484 Heimann, J., see Chełkowski, A. 148, 169, 174-176 Heimann, J., see Drzazga, Z. 148, 169, 174-176 Heimann, J., see Talik, E. 174, 176 Heinemann, C. 619, 620, 684, 716 Heinmaa, I. 475 Heinmaa, I., see Lütgemeier, H. 479 Heisenberg, W. 629 Helgeson, G., see Tanaka, Y. 25, 30, 31 Hellman, F. 119, 120, 134, 135 Hellmann, H. 642, 645 Hellwege, K.H. 413 Hellwege, K.H., see Bonrath, H. 413 Hellwege, K.H., see Grohmann, I. 319 Helmholdt, R.B. 149, 156, 228, 255 Helmholz, L., see Wolfsberg, M. 317, 685 Henig, E.-Th., see Neiva, A.C. 146, 147 Henriques, R.T., see Gonçalves, A.P. 148, 169 Henry, J.Y., see Tolentino, H. 486 Henry, W.E. 413 Herbst, J.F., see Capehart, T.W. 234 Herlach, F., see de Groot, P. 444

746

Herman, F. 69 Herman, I.P., see Skribanowitz, N. 525, 527, 535 Hermsmeier, B.D., see Farrow, R.F.C. 21 Hermsmeier, B.D., see Wu, Y. 125 Herrmann, G.F., see Hill, R.M. 525 Hervo, J., see Marcerou, J.F. 588 Herzberg, G., see Huber, K.P. 656, 657, 659, 665, 679, 683 Herzog, P., see Krekels, T. 478 Hess, B.A. 613, 637 Hess, B.A., see Chandra, P. 637 Hess, B.A., see Eliav, E. 613, 627 Hess, B.A., see Gleichmann, M.M. 637 Hess, B.A., see Jansen, G. 613, 637 Hess, B.A., see Kaldor, U. 637 Hess, B.A., see Samzow, R. 637 Hess, G. 459, 466, 467 Hessler, J.P., see Harrison, J.P. 346, 428 Heully, J.-L. 638 Heumann, E., see Brede, R. 591 Hewak, D.W. 599 Hewat, A.W., see Cava, R.J. 474, 475 Hibbert, A. 634 Hibino, Y., see Kitagawa, T. 600 Hiebl, K., see Weitzer, F. 146, 202, 203, 205, 206 Hihara, T., see Okamoto, N. 145, 149, 158-160 Hildenbrand, D.L., see Murad, E. 660, 673, 674 Hill, K.O., see Kitagawa, T. 600 Hill, R.M. 525 Hill, R.W., see Bleaney, B. 363, 413, 416 Hinks, D.G., see Broach, R.W. 302, 303, 370, 448 Hinks, D.G., see Dunlap, B.D. 413 Hinks, D.G., see Jorgensen, J.D. 482 Hirayama, F., see Inokuti, M. 553 Hirscher, M., see Yan, X. 119 Hirtz, J.P., see Charasse, M.N. 594 Hirvonen, M.T. 299, 413, 417 Ho, J.C., see Tang, Y.J. 413, 420 Hoang, N.V., see Luong, N.H. 215, 252 Hoare, A., see Lyberatos, A. 130 Hocquet, A., see Carette, P. 660, 666, 667, 669, 671, 673, 676 Hodges, J.A. 322, 387, 390, 391, 413, 475, 483, 485 Hodgson, K.O. 689 Hoekstra, T.H., see Horst, F. 600 Hoffmann, H., see Ertl, L. 90, 106, 108 Hoffmann, R. 650 Hoffmann, R., see Ortiz, J.V. 610, 689, 690 Hoffmann, R., see Rabaâ, H. 610, 703 Hohenberg, P. 641 Hohenberg, P.C., see Aharony, A. 424 Hohlwein, D., see Zeiske, T. 475 Holmes, L.M. 346, 413, 415, 420

Holmes, L.M., see Als-Nielsen, J. 302, 413 Holstein, T. 408 Homborg, H., see Haghighi, M.S. 695 Homma, M., see Okada, M. 209, 228, 232, 233, 237 Homma, Y., see Nakagome, H. 597 Honda, S. 90, 93, 101 Hong, H.Y. 569 Hong, M., see Bohr, J. 30, 54 Hong, M., see Camley, R.E. 20, 65 Hong, M., see Kwo, J. 3, 14, 16, 20-22, 30, 39, 47 Hong, M., see Majkrzak, C.F. 3, 39, 44, 46-48, 54, 60, 65 Hong, M., see van Dover, R.B. 94 Hong, M., see Yafet, Y. 7, 50, 69 Hopster, H.J., see Falicov, L.M. 20, 32, 35, 47 Horiguchi, M., see Hattori, K. 599 Horikoshi, Y., see Yamamoto, Y. 527 Horiuchi, S. 475, 482 Horst, F. 600 Horvitz, E.P. 453 Hosoito, N., see Mibu, K. 90, 113, 114, 121 Hosoito, N., see Yoden, K. 90, 112, 113 Hosoya, H. 611 Hosseini, S.M., see Krekels, T. 478 Hosseini Teherani, F., see Tanabe, K. 487, 488 Hotokka, M. 682 Howard, W.E., see Chang, L.L. 15 Hsieh, T.C., see Majkrzak, C.F. 46 Hu, B., see Huang, R.-W. 253 Hu, B.-P. 148, 156, 215, 221, 250, 251 Hu, B.-P., see Christides, C. 215, 228, 248-250 Hu, B.-P., see Li, H.-S. 215, 248 Hu, C.D. 681, 682 Hu, J. 149, 155, 156, 215, 216, 218, 220, 237, 248, 251 Hu, Y.H., see Guan, W.Y. 413 Huan, C.H.A., see Bleaney, B. 318, 322, 351, 366, 367, 387 Huan, C.H.A., see Wolf, W.P. 429 Huang, C., see Huang, L. 705 Huang, C.Y., see Rachford, F.J. 390, 392 Huang, J.-C. 17, 19 Huang, K. 547 Huang, K., see Born, M. 315, 337 Huang, L. 705 Huang, M.Q., see Wallace, W.E. 261 Huang, R.-W. 253 Huang, S.H. 263 Huang, Y.K., see de Boer, F.R. 228, 255 Huber, A.M., see Charasse, M.N. 594 Huber, A.S., see Kirkwood, A.D. 681 Huber, G., see Brede, R. 591

Huber, K.P. 656, 657, 659, 665, 679, 683 Hubert, S. 534, 535 Hubert, S., see Auzel, F. 532-535, 558 Hufner, S., see Bonrath, H. 413 Huggins, R.A., see Beyers, R. 474, 475 Huiskamp, W.J., see Blöte, H.W.J. 413 Huiskamp, W.J., see Lagendijk, E. 408, 413 Huiskamp, W.J., see Mennenga, G. 346, 413, 420 Huiskamp, W.J., see Steiger, J.J.M. 69 Huiskamp, W.J., see Veenendaal, E.J. 305, 366, 367, 413 Hull Jr, G.W., see Bucher, E. 305 Hull Jr, G.W., see Holmes, L.M. 413, 415 Hulliger, F., see Brände, H. 150, 270 Hulliger, F., see Gueramian, M. 154, 156, 242, 243, 246, 268, 273 Hulling, F., see Allenspach, P. 318, 323 Hulsing, H. 346, 413, 418 Humer, W.F., see Grubb, S.G. 592 Hundley, M.F. 413 Hung, M.P., see Chin, T.S. 209, 215, 228, 232, 237 Hunt, N.E.J., see Schubert, E.F. 600 Hunter, B.A., see Jorgensen, J.D. 482 Hurley, D.P.F. 261, 263 Hurley, D.P.F., see Coey, J.M.D. 261 Hurley, M.M. 646 Huron, B. 648 Huser, D., see Dirkmaat, A.J. 459, 469-471 Husson, D., see Gouedard, C. 538, 539 Huster, M., see Griffin, J.A. 425 Hutchings, M.T. 308, 324, 343, 387, 390, 392 Hutchison Jr, C.A., see Baker, J.M. 391, 444 Hutchison Jr, C.A., see Bleaney, B. 366, 367 Huzinaga, S. 644 Huzinaga, S., see Barandiarán, Z. 639, 644 Huzinaga, S., see Bonifacic, V. 639, 644 Huzinaga, S., see Sakai, Y. 639, 644 Huzinaga, S., see Seijo, L. 644 Iandelli, A. 145, 160, 161 Ibarra, M.R., see Algarabel, P.A. 228 Ibarra, M.R., see Arnold, Z. 228, 252 Ibarra, M.R., see Garcia, L.M. 215 Ibarra, M.R., see Moze, O. 228, 248 Ibarra, M.R., see Pareti, L. 228, 229, 232, 244, 245, 248 Ibberson, R.M., see Moze, O. 157, 167, 168, 176, 209 Ibrahim, H., see Ronarc'h, D. 588, 589 Ichiki, S.K., see Hill, R.M. 525 Ido, H., see Ohashi, K. 216, 233 Igarashi, H., see Kubo, Y. 478 Igel-Mann, G. 647

Igota, K., see Yamamoto, Y. 527 Ihringer, J. 305, 367 Ikunishi, S., see Haruna, M. 599 Ilias, A.I., see Sokolovskaya, E.M. 157 Iliev, M. 475 Imbert, P., see Hodges, J.A. 413, 475, 483, 485 Inokuti, M. 553 Inoue, T., see Suzuki, H. 382, 400 Ioffe, V.A. 359, 360 Ioffe, V.A., see Andronenko, S.I. 359, 391 Iroulart, G., see Brandel, V. 577 Isaacs, E.D. 6, 10, 13, 16 Isaacs, E.D., see Gibbs, D. 6, 10, 13, 16 Isago, H. 695 Ishida, S. 258 Ishida, S., see Asano, S. 259 Ishida, T., see Claus, H. 478 Ishigaki, T. 318, 323 Ishikawa, Y. 635, 643 Ishikawa, Y., see Eliav, E. 613, 627, 635, 651, 652, 669 Ishikawa, Y., see Hafner, P. 622 Ishimoto, H. 400 Islam, M.S. 475, 476 Isnard, O., see Tomey, E. 237, 261 Itoh, T. 637 Itzykson, C. 629 Ivanenko, Z.I., see Malkin, B.Z. 314 Ivanov, A.A., see Popenko, N.I. 686 Ivanov, M.A. 459, 460 Ivanova, G.V., see Ermolenko, A.S. 154, 155, 207, 209, 233, 234, 237, 249, 250 Ivanova, G.V., see Scherbakova, Ye.V. 237, 238, 248 Ivanova, T.I., see Zolotukhin, O.A. 218 Jackson, D.J., see Carlson, N.W. 536 Jacobsen, B., see Shan, Z.S. 125 Jacobson, D.C., see Adler, D.L. 598 Jacobson, D.C., see Schubert, E.F. 600 Jacquier, B., see Joubert, M.F. 511 Jacquier, B., see Lin, G.K. 535 Jacquinot, J.F., see Roinel, Y. 386 Jaeger, H.M., see Mogilevsky, R. 489 Jahns, V. 649, 703, 717 Jakelski, J., see Mensinger, H. 413, 419 Jakelski, J., see Muller, A.U. 419 Jakubovics, J.P., see Sun, H. 265 James, W.J., see Yang, Y.C. 233 Janczak, J., see Suski, W. 150, 234, 268, 272, 273, 279, 280, 282, 283 Jankowski, K. 636 Janossy, A., see Pekker, S. 472, 475, 479, 480, 483

748
Janossy, A., see Rockenbauer, A. 472, 475, 479, 480. 483 Jansen, G. 613, 637 Jansen, G., see Samzow, R. 637 Janssen, P. 444 Jasien, P.G., see Stevens, W.J. 647 Jaskólski, W., see Kobus, J. 640 Jaskorzynska, B., see Blixt, P. 593 Jaswal, S.S. 120, 254-256, 258 Jaswal, S.S., see Fernando, A.S. 215, 228, 232, 258 Jaswal, S.S., see Kusov, A.A. 133 Jaswal, S.S., see Sellmyer, D.J. 140 Jaswal, S.S., see Shan, Z.S. 98, 99, 105, 116-118, 121, 122, 124 Jauncey, J.M., see Mears, R.J. 587 Jauncey, J.M., see Reekie, L. 587 Jayanetti, J.K.D., see Kamprath, N. 264, 266 Jaynes, E.T. 521 Jean-Louis, A.M., see Auzel, F. 595, 598 Jeffries, C.D., see Larson, G.H. 319, 393 Jeffries, C.D., see Scott, P.L. 393 Jeffries, C.D., see Wolfe, J.P. 457 Jehan, D.A. 25, 54 Jehan, D.A., see McMorrow, D.F. 46, 63 Jehan, D.A., see Simpson, J.A. 46, 65 Jehanno, G., see Hodges, J.A. 413, 475, 483, 485 Jelonek, J. 194, 195 Jen, S.U., see Navarathna, A. 160 Jenkins, A.A., see Abraham, M.M. 445 Jensen, J. 4, 7, 9, 30 Jensen, J., see Bohr, J. 30, 54 Jensen, J., see Leask, M.J.M. 415, 416 Jensen, S.J.K. 418, 458 Jerowska, B., see Str,ek, W. 569 Jia, Y.Q. 651, 703, 717 Jia, Y.Q., see Lohr, L.L. 610, 650, 684, 685 Jia, Y.X., see Clinton, T.W. 413, 422 Jiang, H.-W., see Lin, C. 209, 271, 272, 278 Jilek, E., see Roessli, B. 413 Jin, C., see Chai, Y. 696, 699 Jin, L., see Yang, Y.-C. 216 Jin Han-min, see Yan Yu 244 Johansson, B., see Lander, G.H. 150 Johansson, B., see Trygg, J. 157, 160, 161, 257 Johnson, C.T., see Dyall, K.G. 612, 623, 624, 634, 655 Johnson, D.C., see Kitagawa, T. 600 Johnson, L.F. 510, 549 Johnson, L.F., see Guggenheim, H.G. 591 Johnson, R.D. 699 Johnson, W.R., see Mann, J.B. 634 Johnston, D.C., see Lee, W.C. 487 Johnston, D.C., see Vaknin, D. 479

Jones, D.A., see Cooke, A.H. 413, 420 Jones, E.D. 363, 368 Jones, G.D., see Cockroft, N.J. 559 Jørgensen, C.K. 313, 609, 651, 682 Jørgensen, C.K., see Reisfeld, R. 510 Jørgensen, C.K., see Schäffer, C.E. 651 Jørgensen, C.K., see Weber, J. 610, 706 Jorgensen, J.D. 471, 475, 476, 478, 482, 488 Jorgensen, J.D., see Dunlap, B.D. 413 Joubert, J.C., see Elmaleh, D. 413, 420 Joubert, M.F. 511 Joubert, M.F., see Lin, G.K. 535 Jove, J., see Halevy, I. 186-189, 202 Judd, B.R. 371, 542, 543, 572 Junod, A., see Sanchez, D. 490 Jurczyk, M. 156, 222, 228-231, 233, 240-242, 246-248, 252, 255, 273 Kadomatsu, H., see Fujiwara, H. 148, 169, 174, 175 Kadomatsu, H., see Kamimori, T. 162, 174, 198, 200 Kadomatsu, H., see Liu, W.L. 198 Kagawa, T. 634 Kahle, H.G. 346, 413, 418 Kahle, H.G., see Bischoff, H. 322 Kahle, H.G., see Bohm, W. 322 Kahle, H.G., see Enderle, M. 318, 319 Kahle, H.G., see Gehring, G.A. 346, 413, 417, 419 Kahle, H.G., see Grohmann, 1. 319 Kahle, H.G., see Hess, G. 459, 466, 467 Kahle, H.G., see Hulsing, H. 413, 418 Kahle, H.G., see Kasten, A. 413, 418, 458, 459 Kahle, H.G., see Laugsch, J. 343, 346 Kahle, H.G., see Mensinger, H. 413, 419 Kahle, H.G., see Muller, A.U. 419 Kahle, H.G., see Pilawa, B. 458, 459, 467 Kahn, L.R. 613, 638, 639, 646 Kaiser, W. 510 Kaizu, Y., see Kobayashi, H. 610, 700, 701 Kalbfleisch, H., see Becher, W. 346, 413 Kaldis, E., see Roessli, B. 413 Kaldor, U. 637 Kaldor, U., see Eliav, E. 613, 627, 635, 651, 652, 669 Kaledin, L.A. 665, 666, 668, 669 Kaledin, L.A., see Kulikov, A.N. 667 Kalir, D., see Rosen, M. 14, 59 Kallel, A., see Feuss, H. 304 Kalvius, G.M., see Gal, J. 150, 154, 163, 165, 174, 176–178, 181, 182, 185, 201

Kalvius, G.M., see Halevy, I. 186-189, 202

Kalychak, Ya.M., see Bodak, O.I. 157 Kalychak, Ya.M., see Sysa, L.V. 146 Kamimori, T. 162, 174, 198, 200 Kamimori, T., see Liu, W.L. 198 Kaminskii, A.A. 398, 510, 540, 548, 569, 570, 575-577, 580 Kaminskii, A.A., see Bogomolova, G.A. 317 Kamprath, N. 264, 266 Kamprath, N., see Liu, N.C. 264 Kaneko, T. 209, 215 Kang, J.-D., see Huang, R.-W. 253 Kang, J.H., see Erdos, P. 314 Kankeleit, E., see Barnes, R.G. 318, 323 Kaplan, D.E., see Hill, R.M. 525 Kaplan, M.D. 360 Kaplan, M.D., see Bondar', I.A. 355, 356, 359, 360 Kaplan, M.D., see Ioffe, V.A. 360 Kaplan, M.D., see Sokolov, V.I. 459, 466-468 Kaplan, M.D., see Vasil'ev, A.V. 459, 466, 467 Kaplan, M.D., see Vekhter, B.G. 360, 361, 429 Kappatsch, A. 413 Kappler, J.P., see Baudelet, F. 114 Karlow, M.A., see Cooper, S.L. 477 Karpinski, J., see Roessli, B. 413 Karwowski, J. 640 Kasten, A. 346, 413, 418, 419, 458, 459 Kasten, A., see Battison, J.E. 300, 366, 404 Kasten, A., see Bischoff, H. 322 Kasten, A., see Hess, G. 459, 466, 467 Kasten, A., see Hulsing, H. 346, 413, 418 Kasten, A., see Kahle, H.G. 346, 418 Kasten, A., see Mensinger, H. 413, 419 Kasten, A., see Muller, P.H. 319, 322, 405 Kasten, A., see Pilawa, B. 458, 459, 467 Kasuya, T. 10 Kataev, V., see Braunisch, W. 478 Katila, T.E. 413 Katila, T.E., see Hirvonen, M.T. 299, 413, 417 Kato, T., see Nagase, S. 699, 717 Katter, M. 265 Katter, M., see Schnitzke, K. 266 Katter, M., see Schultz, L. 265, 266 Kaufman, J.J. 682 Kaufman, U. 595 Kaupp, M. 690, 716 Kawaguchi, K., see Yoden, K. 90, 112, 113 Kawarazaki, S., see Suzuki, H. 401, 413 Kazakov, B.N., see Antipin, A.A. 392, 393 Kazakov, B.N., see Bumagina, L.A. 324, 415 Kazakov, B.N., see Davidova, M.P. 318, 322-324 Kazei, Z.A. 301, 361, 413, 429 Kazei, Z.A., see Abdulsabirov, R.Yu. 336, 350 Kazei, Z.A., see Bondar', I.A. 355, 356, 359, 360

Kazei, Z.A., see Sokolov, V.I. 350, 351, 459, 466-468 Kazei, Z.A., see Vasil'ev, A.V. 459, 466, 467 Kazei, Z.A., see Vekhter, B.G. 361, 429 Kebe, B., see Yang, Y.C. 233 Keen, B.E., see Landau, D.P. 413 Keenan, T.K., see Thoma, R.E. 302 Keffer, F., see Cohen, M.H. 408 K,epiński, L. 151, 279 Kerdiles, J.K., see Clescla, B. 588 Kess, G., see Pilawa, B. 458, 459, 467 Ketelaar, J.A.A. 301 Kettler, P., see Dirkmaat, A.J. 459, 469-471 Keune, W., see Badía, F. 110 Keune, W., see Scholz, B. 109, 111, 112 Khabrov, V.I., see Scherbakova, Ye.V. 237, 238, 248 Khachaturyan, A.G. 473 Khachaturyan, A.G., see Semenovskaya, S. 473, 474, 477 Kharchenko, N.F., see Beznosov, A.B. 150, 273 Khasanov, A.Kh., see Al'tshuler, S.A. 363, 365, 386 Khasanov, A.Kh., see Bumagina, L.A. 323, 324, 352, 431, 434 Khat'sko, E.N. 413 Khmel'nitskii, D.E., see Larkin, I.A. 423 Khomskii, D., see Braunisch, W. 478 Khutsishvili, G.R. 384 Kido, G., see Kaneko, T. 209, 215 Kiel, A. 545 Kikuchi, R. 473 Kilner, J.A., see Bredikhin, S.I. 477 Kim, S., see Lee, W.C. 487 Kim, S., see Phillips, N.E. 490 Kim, Y.K. 634 Kim-Ngan, N.H. 168 Kimura, T., see Honda, S. 101 Kimura, Y., see Nakazawa, M. 599 Kindstedt, T., see Hotokka, M. 682 King, A.R. 456 Kinsley, S.A., see Streitwieser, A. 610, 689, 691 Kintz, G.J. 557 Kirby, R.D. 83, 105, 125, 128-131 Kirby, R.D., see Sellmyer, D.J. 140 Kirby, R.D., see Shan, Z.S. 91 Kircher, J., see Hadjiev, V.G. 476, 489 Kirchmayr, H.R. 145 Kirino, F., see Suzuki, Y. 119 Kirkwood, A.D. 681 Kirschbaum, U., see Scholz, B. 109, 111, 112 Kissel-Phillip, M., see Schwarz, W.H.E. 638 Kitagawa, T. 599, 600 Kitagawa, T., see Hattori, K. 599

Kitaura, K., see Ohta, K. 643 Kittel, C. 403, 578 Kivelson, S.A. 479 Kivelson, S.A., see Emery, V.J. 479 Kjaer, K. 458, 470 Kjaer, K., see Jensen, S.J.K. 418, 458 Kjems, J.K., see Birgeneau, R.J. 365 Kjems, J.K., see Cohen, E. 365 Klafter, J. 488 Klauder, J.R. 486 Klavins, P., see Rosov, N. 413 Kleemann, W., see Wang, Y.J. 82, 125, 136-138 Klein, L., see Kahle, H.G. 413 Klein, M.V., see Cooper, S.L. 477 Klein, M.V., see Flynn, C.P. 47 Klein, O. 640 Klein, P.B., see Pomrenke, G.S. 599 Kleiner, R.K. 478 Kleinman, L. 643 Kleinman, L., see Phillips, J.C. 642 Klemens, P.G. 577, 578 Klemm, R.A., see Lee, W.C. 487 Klemperer, W., see Berg, R.A. 665 Klimker, H., see Rosen, M. 14, 59 Klobukowski, M. 639, 644 Klobukowski, M., see Huzinaga, S. 644 Klobukowski, M., see Sakai, Y. 639, 644 Klochkov, A.V., see Krjukov, E.V. 479, 488, 489 Klofer, P., see Kasten, A. 458, 459 Knappe, P. 696 Knappe, P., see Culberson, J.C. 610, 613, 649, 685, 686, 688, 703 Knauf, N., see Braunisch, W. 478 Knoll, K.D. 319 Knülle, M., see Attenkofer, K. 114, 115 Kobayashi, H. 610, 700, 701 Kobayashi, K. 718 Kobayashi, K., see Nagase, S. 699, 700, 717 Kobayashi, M., see Kitagawa, T. 599 Kobetz, M.I., see Khat'sko, E.N. 413 Kobus, J. 640 Kobus, J., see Karwowski, J. 640 Kobyliansky, A.I., see Kulikov, A.N. 667 Koch, M.E. 564, 593 Koch, M.E., see Case, W.E. 561 Koch, M.E., see Kueny, A.W. 561, 562 Koch, W. 682 Kochelaev, B.I., see Aminov, L.K. 312 Kock, A., see Braunisch, W. 478 Kockelmann, W. 154, 185-188, 413 Kockelmann, W., see Schäfer, W. 185 Koehler, W.C. 10 Koelling, D.D. 622 Koetke, J., see Brede, R. 591

Köhl, F., see Kaufman, U. 595 Kohn, J.L., see Osofsky, M.S. 478 Kohn, W. 641, 700 Kohn, W., see Hohenberg, P. 641 Kojima, A., see Okada, M. 209, 228, 232, 233, 237 Kolmakova, N.P. 413 Kolmakova, N.P., see Kazei, Z.A. 301, 361, 413 Kolmakova, N.P., see Sokolov, VI. 350, 351 Komukai, T. 592 Komura, Y., see Ohashi, K. 157, 215, 218, 221 Kong, L.-S., see Ge, S.-L. 209, 215 Kong, L.-S., see Yang, Y.-C. 216, 261 Kong, L.S., see Cao, L. 215 Kong, L.S., see Yang, Y.-C. 215, 243, 245 Kong, S.H., see Flynn, C.P. 47 Konno, K., see Ohashi, K. 216, 233 Konov, I.S. 363, 365, 368, 382 Konov, I.S., see Abdulsabirov, R.Yu. 364 Konov, I.S., see Antipin, A.A. 382, 384, 385, 390, 392 Konov, I.S., see Aukhadeev, F.L. 368, 377, 382 Konov, I.S., see Eremin, M.V. 369, 371, 372 Koon, N.C., see Harris, V.G. 119, 120, 140 Korableva, S.L. 362, 364, 387 Korableva, S.L., see Abdulsabirov, R.Yu. 336, 350, 357, 364, 433 Korableva, S.L., see Al'tshuler, S.A. 354, 434, 435 Korableva, S.L., see Aminov, L.K. 300, 390, 392, 393, 396, 397 Korableva, S.L., see Antipin, A.A. 382, 384, 385, 390, 392, 393 Korableva, S.L., see Davidova, M.P. 318, 323 Korableva, S.L., see Vinokurov, A.V. 338, 339 Korecz, L., see Rockenbauer, A. 472, 475, 479, 480, 483 Koreiba, M.A., see Aminov, L.K. 300, 397, 399, 461, 469 Koreiba, M.A., see Malkin, B.Z. 352, 460, 470 Kornblit, A., see Ahlers, G. 424, 425 Korovkin, A.M., see Vinokurov, A.V. 322, 338, 339 Kosterlitz, J.M. 34 Kostetskii, Yu.Yu. 318, 324 Kostetskii, Yu.Yu., see Aminov, L.K. 300, 390, 392, 393, 396, 397, 399 Kostikas, A., see Christides, C. 209, 215, 228, 234, 237, 248-250, 253, 259, 261, 273 Köstlmeier, S., see Cory, M.G. 614, 649 Köstlmeier, S., see Jahns, V. 649, 703, 717 Koterlin, M.D. 167, 174, 181, 182 Koterlin, M.D., see Shcherba, I.D. 151-153, 163, 165, 167, 168, 174, 175, 181, 182

Kotz, A., see Cooper, S.L. 477 Kotzian, M. 613, 648, 649, 663, 665, 666, 668, 669, 675, 676, 701, 702, 717 Kotzian, M., see Cory, M.G. 614, 649 Kotzian, M., see Jahns, V. 649, 703, 717 Kotzler, J. 405, 425 Kotzler, J., see Frowein, R. 417, 424, 425 Kotzler, J., see Grahl, M. 405 Kou, X.C., see Christides, C. 237, 273 Kowalczyk, A., see Stefański, P. 209, 232, 233, 244, 247, 252, 253 Kozhevnikov, V., see Podlesnyak, A. 318 Kozyrev, B.M., see Al'tshuler, S.A. 297, 308, 374, 378, 386, 450 Krabbes, G., see Heinmaa, I. 475 Krajewski, J.J., see Cava, R.J. 474, 475 Kramer, M., see Lunkenheimer, P. 185 Kramer, M.J., see Allenspach, P. 413, 422 Krasnov, K.S. 686 Krasutsky, N.J. 561 Krauns, C. 475 Krauss, M. 646 Krauss, M., see Stevens, W.J. 647 Kravchenko, I.I., see Shcherba, I.D. 151-153, 163, 165, 167, 168, 174, 175, 181, 182 Kravchenko, S.V., see Ioffe, V.A. 360 Krebs, H.-U., see Krauns, C. 475 Krebs Larsen, F., see Kjaer, K. 458, 470 Krekels, T. 478 Krekels, T., see Reyes-Gasga, J. 474, 475, 478 Krewenka, R., see Grössinger, R. 228, 246 Krill, G., see Baudelet, F. 114 Krill, G., see Tolentino, H. 486 Krimmel, A. 150, 152, 154, 162, 181, 183, 184, 189 Kripyakevich, P.I., see Kuz'ma, Yu.B. 161 Kripyakevich, P.I., see Zarechnyuk, O.S. 146, 148, 157 Kristofel', N.N. 397 Krjukov, E.V. 479, 488, 489 Krjukov, E.V., see Bakharev, O.N. 479, 488, 489 Krjukov, E.V., see Ishigaki, T. 318, 323 Krjukov, E.V., see Teplov, M.A. 479, 487, 489 Kroll, N.M., see Douglas, M. 637, 641 Kropotova, T.V., see Aminov, L.K. 441, 445, 448, 452, 454, 455 Kroto, H.W. 695 Kroto, H.W., see Zhang, Q.L. 696 Krotov, V.I. 431, 435 Krotov, V.I., see Al'tshuler, S.A. 354-356, 434, 435 Krotov, V.I., see Bumagina, L.A. 323, 324, 352, 431, 434 Krupa, J.C., see Gérard, I. 715, 716

Krupke, W.F., see De Loach, L.D. 549 Krygin, I.M. 456 Krynetskii, I.B., see Kolmakova, N.P. 413 Ku, H.C., see Chin, T.S. 209, 215, 228, 232, 237 Ku, H.C., see Tang, Y.J. 413, 420 Kuang, J.-P., see Yang, F.-M. 232, 233, 248, 249 Kubo, S., see Tanabe, K. 487, 488 Kubo, Y. 478 Kubota, M. 400 Kubota, M., see Folle, H.R. 400 Küchle, W. 613, 618, 619, 623, 625, 640, 647, 670 Küchle, W., see Bergner, A. 647 Küchle, W., see Dolg, M. 629, 647, 654, 655, 692, 693, 716 Kudrevatykh, N.V. 249 Kudrevatykh, N.V., see Andreev, A.V. 148, 215, 221, 222, 245, 246, 248-250 Kudrevatykh, N.V., see Deryagin, A.V. 270 Kudryashov, A.A., see Al'tshuler, S.A. 361, 362 Kudryashov, A.A., see Aminov, L.K. 368, 379, 383, 384 Kudryashov, A.A., see Egorov, A.V. 370, 373, 376, 377 Kueny, A.W. 561, 562 Kueny, A.W., see Case, W.E. 561 Kueny, A.W., see Koch, M.E. 564, 593 Kuhn, H.G. 550 Kuhrt, C., see Schultz, L. 266 Kulikov, A.N. 667 Kunitomi, N., see Suzuki, H. 401, 413 Kupchikov, A.K. 318, 321, 338, 404 Kuric, M.V., see Bulman, J.B. 413 Kurkin, I.N. 475 Kurkin, I.N., see Aminov, L.K. 300, 388, 390, 392, 393, 396, 397 Kurkin, I.N., see Eremin, M.V. 325 Kurkin, I.N., see Korableva, S.L. 387 Kurnit, N.A. 526, 531 Kurti, N. 399 Kurtz, R., see Fillion, G. 413, 428 Kushida, T. 551, 576 Kushida, T., see Yamada, N. 553 Kushnir, A.P., see Shcherba, I.D. 151-153, 163, 165, 167, 168, 174, 175, 181, 182 Kusov, A.A. 133 Kustov, E.F. 572 Kusuda, T., see Honda, S. 90, 93, 101 Kutzelnigg, W. 609, 629, 636 Kutzelnigg, W., see Ottschofski, E. 636 Kutzelnigg, W., see Wallmeier, H. 638 Kuz'ma, Yu.B. 146, 154, 161 Kuz'ma, Yu.M., see Stelmakhovich, B.M. 146, 154

Kuz'min, M.D., see Garcia, L.M. 215 Kvitnickaya, O.E., see Naydyuk, Yu.G. 151, 181, 183, 189 Kway, W.L., see De Loach, L.D. 549 Kwo, J. 3, 14, 16, 20–22, 30, 39, 47 Kwo, J., see Bohr, J. 30, 54 Kwo, J., see Camley, R.E. 20, 65 Kwo, J., see Majkrzak, C.F. 3, 39, 44, 46-48, 54, 60, 65 Kwo, J., see Yafet, Y. 7, 50, 69 Kwo, R.J. 20 Kwok, W.K., see Dunlap, B.D. 413 Kwok, W.K., see Jorgensen, J.D. 475, 478 Laakkonen, L.J., see Pyykkö, P. 684 Laasonen, K. 699 Lagendijk, E. 408, 413 Lagorsse, O., see Charasse, M.N. 594 LaJohn, L.A. 646 LaJohn, L.A., see Ross, R.B. 646 Lallier, E. 599 Lallier, E., see Li, M.J. 580, 599 Lambeck, P.V., see Horst, F. 600 Lambert, B. 596 Lambert, B., see Lhomer, C. 596 Lambert, B., see Rochaix, C. 594 Lambert, B., see Rolland, A. 595, 596 Lambeth, D.N., see Falicov, L.M. 20, 32, 35, 47 Laming, R.J., see Hewak, D.W. 599 Lan, G. 705, 717 Landau, D.P. 413 Lander, G.H. 150 Lang, H.Y., see Quezel, G. 413 Langer, D.W., see Pomrenke, G.S. 599 Langer, J.M. 596 Langhoff, S.R. 652, 657 Langreth, D.C., see Hu, C.D. 681, 682 Lankard, J.R., see Sorokin, P.R. 510 Lanza, G., see DiBella, S. 684, 688, 716 Large, A.C., see Chartier, I. 600 Large, A.C., see Sheperd, D.P. 600 Larkin, I.A. 423 Larsen, F.K., see Als-Nielsen, J. 302, 413 Larson, G.H. 319, 393 Larsson, S. 650 Lasjaunias, J.C., see Filippi, J. 413 Lauder, R.D.T. 590 Lauder, R.D.T., see Percival, R.M. 590 Laughlin, D.E., see Cheng, S.F. 218 Laugsch, J. 343, 346 Laursen, I., see Beauvillain, P. 346, 424, 425, 468 Laursen, I., see de Groot, P. 444 Laursen, I., see Janssen, P. 444 Laursen, I., see Kjaer, K. 458, 470

Laursen, I., see Magarino, J. 426, 444 Laursen, I., see Mennenga, G. 346, 420, 458, 468, 469 Laursen, I., see Pommier, J. 404 Lavizina, O.V., see Ishigaki, T. 318, 323 Lavrov, A.N. 477 Lazzouni, M., see Bleaney, B. 318, 322, 363, 366, 367, 416 Le Corre, A., see Favennec, P.N. 594 Le Corre, A., see Lambert, B. 596 Le Corre, A., see Lhomer, C. 596 Le Corre, A., see Rolland, A. 595, 596 Le Corre, H., see Rochaix, C. 594 Le Roy, J. 263 Leask, M.J.M. 413, 415, 416, 429 Leask, M.J.M., see Baker, J.M. 391, 444 Leask, M.J.M., see Battison, J.E. 300, 366, 404 Leask, M.J.M., see Bleaney, B. 318, 322, 363, 364, 366, 367, 408, 413, 416, 429 Leask, M.J.M., see Brown, P.J. 413, 416 Leask, M.J.M., see Cashion, J.D. 408, 413 Leask, M.J.M., see Cooke, A.H. 413 Leask, M.J.M., see Hawkes, J.F.B. 343 Leask, M.J.M., see Wolf, W.P. 413 Leavitt, R.P., see Morrison, C.A. 301, 312 Leciejewicz, J., see Ptasiewicz-B, ak, B. 150, 176, 177, 181-183, 190, 194, 195 Lecronier, D., see Rolland, A. 595, 596 Lee, B.W., see Allenspach, P. 413, 422 Lee, B.W., see Clinton, T.W. 422 Lee, B.W., see Yang, K.N. 413 Lee, H.T., see Chin, T.S. 209, 215, 228, 232, 237 Lee, S.Y. 648 Lee, V.Y., see Beyers, R. 474, 475 Lee, W.C. 487 Lee, W.C., see Cooper, S.L. 477 Lee, Y.S. 647 Lee, Y.S., see Baeck, K.K. 635 Lee, Y.S., see Bagus, P.S. 626, 627 Lee, Y.S., see Christiansen, P.A. 646 Lee, Y.S., see Lee, S.Y. 648 Leempoels, F., see de Groot, P. 444 Leggieri, G., see Cosmovici, C.B. 673, 674 Leibfried, G. 577 Lemaire, F., see Charasse, M.N. 594 Lemaire, R., see Deportes, J. 145 Lempicki, A. 510 Lenth, W. 561, 564 Lenth, W., see Hebert, T. 564, 591 Lenth, W., see Macfarlane, R.M. 591 Lenth, W., see Tong, F. 591 Leson, A., see Purwins, H.G. 301 Levi-Setti, R., see Mogilevsky, R. 489 Lewis, V.G., see O'Grady, K. 127

Lewis, W.A., see Fahrle, M. 35 Leyland, P.C., see Linton, C. 667, 668 L'Haridon, H., see Barrière, A.S. 600 L'Haridon, H., see Favennec, P.N. 594, 597 L'Haridon, H., see Rochaix, C. 594 L'Haridon, H., see Rolland, A. 595, 596 Lhomer, C. 596 Lhomer, C., see Lambert, B. 596 Li, D.Q. 35 Li, G.Z., see Lin, C. 209, 271, 272, 278 Li, H., see Yang, Y.-C. 261 Li, H.-S. 148, 215, 248, 249 Li, H.-S., see Christides, C. 259, 261 Li, H.-S., see Hu, B.-P. 148, 156, 215, 251 Li, H.-S., see Otani, Y. 265 Li, H.S., see Cadogan, J.M. 203 Li, H.S., see Christides, C. 209, 215, 228, 248-250, 253 Li, H.S., see Hu, B.-P. 221, 250, 251 Li, J. 610, 695 Li, L. 610, 613, 649, 685, 706 Li, L., see Li, Z. 610, 705 Li, L., see Ren, J. 610, 613, 649, 705 Li, M., see Cao, Y. 705 Li, M.J. 580, 599 Li, M.J., see Lallier, E. 599 Li, Q. 209, 210, 218, 247, 249, 269 Li, Q.-A., see Yang, F.-M. 232, 233, 248, 249 Li, Q.-A., see Yang, H. 229, 230, 251 Li, S., see Van Zee, R.J. 680 Li, W.-H., see Skanthakumar, S. 413 Li, W.-H., see Yang, K.N. 413 Li, X., see Zhao, Z.G. 135 Li, Y., see Yang, H. 229, 230, 251 Li, Y.P., see Qi, Q.-N. 263 Li, Z. 610, 705 Li, Z., see Lan, G. 705, 717 Li, Z.W. 218, 219, 222 Li Lin, see Mogilevsky, R. 489 Liao, L.X. 261 Liberman, A.B., see Zhdanov, R.Sh. 367 Lidskii, B.V., see Aleksandrov, I.V. 435 Lightfoot, P., see Jorgensen, J.D. 471, 476, 482, 488 Lin, C. 209, 271, 272, 278 Lin, C.-H., see Huang, S.H. 263 Lin, G.K. 535 Lin, H., see Rebelsky, L. 272 Lin, H.Q., see Emery, V.J. 479 Lin, H.Q., see Kivelson, S.A. 479 Lindgren, I. 612, 634 Lindgren, I., see Heully, J.-L. 638 Lindgren, I., see Judd, B.R. 371 Lindroth, E., see Heully, J.-L. 638

Lines, M.E. 427 Linker, G., see Claus, H. 478 Linton, C. 667, 668, 672-674 Linton, C., see McDonald, S.A. 651, 673, 675 Liou, S.H., see Shan, Z.S. 125 Lipscomb, W.N., see Hoffmann, R. 650 Lipscomb, W.N., see Lohr, L.L. 650 Lischka, H., see Mark, F. 635 Litster, J.D., see Griffin, J.A. 404, 423, 425 Litterst, F.J., see Gal, J. 150, 154, 163, 165, 174, 176-178, 181, 182, 185, 201 Liu, B., see Froese Fischer, C. 634 Liu, J.P., see Yang, F.-M. 232, 233, 248, 249 Liu, J.Z., see Clinton, T.W. 413, 422 Liu, N.C. 264 Liu, N.C., see Kamprath, N. 264, 266 Liu, R., see Cooper, S.L. 477 Liu, S.H. 9 Liu, S.H., see Evenson, W.E. 9 Liu, W.-L., see Fujiwara, H. 148, 169, 174, 175 Liu, W.L. 198 Liu, W.L., see Kamimori, T. 162, 174, 198, 200 Liu, Y., see Hu, J. 218 Liu, Y., see Zhang, Q.L. 696 Liu, Y.C., see Linton, C. 672-674 Liu, Y.J., see Callen, E. 137, 138 Liu, Z.-X., see Lin, C. 209, 271, 272, 278 Livanova, L.D., see Egorov, A.V. 363, 366-368 Livanova, L.D., see Tagirov, M.S. 364, 366 Lloyd, R.G. 471 Loew, L.M., see Myers, C.E. 610, 685 Logan, R.A., see Tsang, W.T. 597, 598 Logan, R.A., see Van der Ziel, J.P. 597 Lohmuller, G. 304 Lohneysen, H., see Riedling, S. 478 Lohr, L.L. 610, 613, 650, 684, 685 Lohr, L.L., see Pyykkö, P. 610, 650, 685 Loidl, A., see Krimmel, A. 150, 152, 154, 162, 181, 183, 184, 189 Loidl, A., see Lunkenheimer, P. 185 Loong, C.-K. 318, 319, 321, 322 Lopez, J.P., see Case, D.A. 610, 706 Lord, A., see Boggis, J.M. 588 Lottis, D.K. 130 Lowry, J.B., see Battison, J.E. 300, 366, 404 Lowry, J.B., see Cooke, A.H. 413 Lu, Y., see Li, Q. 209, 210, 218, 247, 249, 269 Luche, M.C. 21, 61, 64, 65 Lucht, R., see Riedling, S. 478 Luciński, T., see Lunkenheimer, P. 185 Ludeke, R., see Chang, L.L. 15 Ludwig, H.A., see Metzger, J. 477 Lugiato, L.A., see Bonifacio, R. 512, 524, 526-528, 530

754

Luis, F. 237, 238, 252 Luis, F., see Garcia, L.M. 237-239, 246, 247, 252 Łukasiak, M., see Baran, A. 267, 268, 271, 273 Lukin, S.N., see Abdulsabirov, R.Yu. 364 Lukin, S.V., see Korableva, S.L. 387 Lukina, M.M., see Kolmakova, N.P. 413 Lukowiak, E., see Str, ek, W. 569 Lundqvist, S., see Heully, J.-L. 638 Lunkenheimer, P. 185 Luo, T., see Yang, Y.-C. 218, 219, 222, 243 Luong, N.H. 215, 252 Lütgemeier, H. 479 Lütgemeier, H., see Bakharev, O.N. 318, 323, 479 Lütgemeier, H., see Dooglav, A.V. 484, 485 Lütgemeier, H., see Egorov, A.V. 479, 483-485 Lütgemeier, H., see Heinmaa, I. 475 Luttinger, J.M. 407 Lyberatos, A. 130 Lynn, J.W. 413 Lynn, J.W., see Clinton, T.W. 413, 422 Lynn, J.W., see Rosov, N. 413 Lynn, J.W., see Skanthakumar, S. 413 Lynn, J.W., see Yang, K.N. 413 Lynn, J.W., see Zhang, H. 413, 421 Lyons, K.B. 365 Ma, R.H. 209, 228, 247 Ma, R.Z., see Geng, M.M. 237 MacChesney, J.B. 413 MacDonald, A.H., see Koelling, D.D. 622 591 Macfarlane, R.A., see Stephens, R.R. Macfarlane, R.M. 531, 553, 591 Macfarlane, R.M., see Genack, A.Z. 531 Macfarlane, R.M., see Glynn, T.J. 458, 467 Macfarlane, R.M., see Hebert, T. 564, 591 Macfarlane, R.M., see Lenth, W. 561, 564 Macfarlane, R.M., see Shelby, R.M. 531 Macfarlane, R.M., see Tong, F. 591 Macfarlane, R.M., see Wannemacher, R. 531 MacGillivray, J.C. 525, 529 MacGillivray, J.C., see Skribanowitz, N. 525, 527, 535 Machida, S., see Yamamoto, Y. 527 Maciel, G.S., see Gomes, A.S.L. 562 MacIsaac, A.B. 421 Mackintosh, A.R., see Jensen, J. 4, 7, 9, 30 Mackrodt, W.C. 634 Madeore, F., see Vial, J.C. 559 Magarino, J. 426, 444 Magarino, J., see Beauvillain, P. 321, 420 Maiman, T.H. 510 Maitre, H., see Cozannet, A. 582 Majkrzak, C.F. 3, 39, 44, 46-48, 54, 60, 65 Majkrzak, C.F., see Bohr, J. 30, 54

Majkrzak, C.F., see Kwo, J. 21, 22, 30, 47 Majkrzak, C.F., see Yafet, Y. 7, 50, 69 Maketov, T.K., see Kustov, E.F. 572 Maki, J.J., see Malcuit, M.S. 528, 532 Malcuit, M.S. 528, 532 Malhotra, V.M. 392 Mali, M., see Brinkmann, D. 475 Maliepaard, M., see Graham, J.T. 459 Malik, S.K. 174, 175 Malik, S.K., see Dunlap, B.D. 413 Malik, S.K., see Sinha, V.K. 215, 218 Malikov, R.F. 529, 533 Malkin, B.Z. 312, 314, 317, 328, 352, 427, 460, 470 Malkin, B.Z., see Abdulsabirov, R.Yu. 357, 433 Malkin, B.Z., see Al'tshuler, S.A. 310, 350, 352-356, 389, 434, 435 Malkin, B.Z., see Aminov, L.K. 300, 397, 399, 461, 469 Malkin, B.Z., see Andronenko, S.I. 359 Malkin, B.Z., see Aukhadeev, F.L. 431 Malkin, B.Z., see Avanesov, A.G. 323, 324 Malkin, B.Z., see Bogomolova, G.A. 317 Malkin, B.Z., see Bumagina, L.A. 323, 324, 352, 415, 431, 434 Malkin, B.Z., see Hirvonen, M.T. 299, 413, 417 Malkin, B.Z., see Krotov, V.I. 431, 435 Malkin, B.Z., see Kupchikov, A.K. 318, 321, 338, 404 Malkin, B.Z., see Vinokurov, A.V. 322, 338, 339 Malli, G.L. 612, 635 Malli, G.L., see Ishikawa, Y. 643 Malli, G.L., see Matsuoka, O. 635 Malo, B., see Kitagawa, T. 600 Malozemoff, A.P. 149, 259 Malozemoff, A.P., see Bulaevskii, L.N. 478 Malozemoff, A.P., see Williams, A.R. 259 Malrieu, J.P., see Huron, B. 648 Malrieu, J.P., see Teichteil, C.H. 613 Malta, O.L. 600 Malta, O.L., see Auzel, F. 571, 572, 595 Mamsurova, L.G., see Aleksandrov, I.V. 435 Mangin, Ph., see Cherifi, K. 109-111 Mangum, B.W., see Colwell, J.H. 346, 413 Mangum, B.W., see Wolf, W.P. 413 Mangum, B.W., see Wright, J.C. 346 Mann, J.B. 612, 634 Manneville, P., see Hammann, J. 413 Manning, D.I., see Harley, R.T. 351, 354, 360 Mansuripur, M. 132 Mansuripur, M., see Fu, H. 120 Mansuripur, M., see Giles, R.C. 132 Mansuripur, M., see Wu, T.-H. 134-136 Maple, M.B., see Allenspach, P. 413, 422

Maple, M.B., see Clinton, T.W. 422 Maple, M.B., see Yang, K.N. 413 Marcerou, J.F. 588 Marchal, G., see Baczewski, C.T. 119 Marchal, G., see Cherifi, K. 109-111 Marchand, R.L. 393 Marchenko, V.M., see Vagin, Y.S. 549 Marcus, M.A., see Adler, D.L. 598 Mares, F., see Hodgson, K.O. 689 Marezio, M., see Cava, R.J. 474, 475 Margarian, A., see Cadogan, J.M. 203 Margrave, J.L., see Hastie, J.W. 687 Marian, C.M. 670 Marian, C.M., see Fleig, T. 638 Marinero, E.E., see Egami, T. 94 Marinero, E.E., see Yan, X. 119 Mark, F. 635, 636 Mark, F., see Schwarz, W.H.E. 620 Markert, J.T., see Edwards, H.L. 475 Marketos, P., see Pyper, N.C. 643 Marks, T.J. 689 Markushev, V.M. 538 Márquez, A. 665, 716 Mårtensson-Pendrill, A.-M., see Heully, J.-L. 638 Martin, D.M., see Cooke, A.H. 413 Martin, R.L. 618, 638 Martin, W.C. 609, 612, 619, 652-654, 671, 682, 701 Martineau, P.M., see Abraham, M.M. 445 Martineau, P.M., see Baker, J.M. 391, 444 Marusi, G., see Pareti, L. 228, 229, 232, 244, 245, 248 Marvin, O.V., see Bakharev, O.N. 472, 479, 481-483, 486-491 Marvin, O.V., see Dooglav, A.V. 484, 485 Marvin, O.V., see Ishigaki, T. 318, 323 Marvin, O.V., see Krjukov, E.V. 479, 488, 489 Marvin, O.V., see Teplov, M.A. 479, 487, 489 Mason, T.M., see Bleaney, B. 408 Massalski, T.B. 17 Masuda, Yu., see Suzuki, H. 401 Matar, S.F. 270, 286 Matheny, A., see Beach, R.S. 21, 22, 24, 25, 30, 45, 46, 59, 62 Matheny, A., see Majkrzak, C.F. 46 Matheny, A., see Reimer, P.M. 16 Matheny, A., see Salamon, M.B. 46, 48, 52, 70 Mathon, J. 70, 71 Matsuoka, O. 635 Matthews, J.W. 26 May, P.S., see Oetliker, U. 561 Mayer, H.M., see Rauchschwalbe, U. 178, 181-183, 195 Mayer, J. 16

Mayers, D.F., see Grant, I.P. 612, 634 Mazurak, Z., see Str,ek, W. 569 McCarron III, E.M., see Emerson, J.P. 490 McCarron III, E.M., see Phillips, N.E. 490 McClure, S.M., see Guo, T. 696 McColl, D.B., see Folinsbee, J.T. 346, 428 McColl, D.B., see Taylor, D.R. 428 McCord, J.E., see Kaledin, L.A. 665, 668, 669 McDaniel, T.W., see Mansuripur, M. 132 McDonald, S., see Linton, C. 672-674 McDonald, S.A. 650, 651, 670, 671, 673, 675 McElfresh, M.W., see Rebelsky, L. 272 McHenry, M.R. 487 McIntyre, G.J., see Krimmel, A. 150, 152, 154, 162, 181, 183, 184, 189 McKenzie, B.J., see Grant, I.P. 612, 634 McMorrow, D.F. 46, 63 McMorrow, D.F., see Jehan, D.A. 25, 54 McMorrow, D.F., see Simpson, J.A. 46, 65 McNiff Jr, E.J., see Bulman, J.B. 413 McWhan, D.B. 15 McWhan, D.B., see Gibbs, D. 6, 10, 13, 16 McWhan, D.B., see Isaacs, E.D. 6, 10, 13, 16 McWhan, D.B., see Kwo, J. 3, 14, 16, 20-22, 30, 39, 47 McWhan, D.B., see Majkrzak, C.F. 39, 44, 46-48, 60 McWhan, D.B., see Vettier, C. 46 Mears, R.J. 580, 587, 591 Medeiros Neto, J.A., see Hewak, D.W. 599 Meekinson, C.D., see Sun, H. 265 Mehran, F. 387, 388, 391, 392, 398 Mehring, M. 475 Meichenin, D., see Auzel, F. 532-535, 558, 559, 563, 586, 588, 593 Meichenin, D., see Hubert, S. 534, 535 Meichenin, D., see Ronarc'h, D. 537, 588 Meichenin, D., see Sheperd, D.P. 600 Meijer, P.H.E., see Niemeijer, Th. 408 Meiser Umar, V., see Cai, Z. 613, 651, 652 Meisner, G.P., see Capehart, T.W. 234 Meissner, H.E., see Catanese, C.A. 343, 346, 413 Meissner, H.E., see Skjeltorp, A.T. 346, 413 Melamed, N.J. 567 Melamud, M. 151, 157 Melamud, M., see Gal, J. 181, 182 Melcher, R.L. 335, 351, 429 Melcher, R.L., see Bonsall, L. 333, 341 Melchior, K., see Becher, W. 346, 413 Meltzer, R.S., see Wannemacher, R. 531 Menken, M.J.V., see Baak, J. 489 Mennenga, G. 346, 413, 420, 458, 468, 469 Menovsky, A.A., see Baak, J. 489 Mensinger, H. 413, 419

Menzinger, M., see Yokozeki, A. 673, 674, 679 Merenga, H., see Andriessen, J. 714, 716 Merenga, H., see Visscher, L. 635 Mesot, J. 323, 475, 478 Mesot, J., see Guillaume, M. 318, 323, 473 Mesot, J., see Podlesnyak, A. 318 Mesot, J., see Roessli, B. 413 Metcalfe, M.J. 413 Metzger, J. 477 Meyer, P., see Pommier, J. 404 Meystre, P., see Fu, H. 120 Mezentsceva, L.P., see Andronenko, S.I. 359 Mezentsceva, L.P., see Bondar', I.A. 355, 356, 359, 360 Mezentsceva, L.P., see Ioffe, V.A. 359, 360 Mibu, K. 90, 113, 114, 121 Mibu, K., see Scholz, B. 109, 111, 112 Mibu, K., see Yoden, K. 90, 112, 113 Michel, J.C. 575 Michel, J.C., see Auzel, F. 568, 574 Michel, J.C., see Budin, J.P. 566 Migus, A., see Gouedard, C. 538, 539 Mikolajczak, P., see Misra, S.K. 392 Mikulyak, R.M., see Van der Ziel, J.P. 557 Mill, B.V., see Vasil'ev, A.V. 459, 466, 467 Mill, B.V., see Vekhter, B.G. 429 Millar, C.A., see Whitley, T.J. 592 Miller, D.C., see Singh, S. 538, 575 Miller, L.L., see Lee, W.C. 487 Miller, M.M., see Fong, F.K. 548 Miller, M.M., see Osofsky, M.S. 478 Miller, R.C. 579 Miller-Vogt, G., see Kahle, H.G. 413 Mills, D., see Gibbs, D. 6, 10, 13, 16 Milner, A.A., see Beznosov, A.B. 150, 273 Min, X. 705, 716 Miora, Y., see Ishimoto, H. 400 Miragha, S., see Tomey, E. 237, 261 Miraglia, S., see Luis, F. 237, 238, 252 Miraglia, S., see Tomey, E. 237 Mirmelstein, A., see Podlesnvak, A. 318 Mishra, R.K., see Capehart, T.W. 234 Misra, S.K. 392, 408, 420 Misra, S.K., see Felsteiner, J. 408 Missel, F.P., see Neiva, A.C. 146, 147 Mitchell, P.W., see Lloyd, R.G. 471 Mitrofanov, V.Ya., see Ivanov, M.A. 459, 460 Mittel'man, A.A., see Krotov, V.I. 431, 435 Miyajima, Y. 590 Miyajima, Y., see Komukai, T. 592 Miyakawa, T. 544-546, 548, 552 Miyamoto, M., see Suzuki, H. 401 Miyamoto, S., see Schutzmann, J. 478 Miyoshi, E., see Sakai, Y. 639, 644

Mizoguchi, T. 120, 125 Mizrahi, V., see Zyskind, J.L. 600 Mobus, G., see Mayer, J. 16 Mochel, M.E., see Durbin, S.M. 15 Mochizuki, K., see Edagawa, E. 587 Mochizuki, K., see Wakabayashi, H. 587 Mogilevsky, R. 489 Mohanty, A.K. 635 Molchanov, V.N., see Voronkova, V.I. 475 Mombelli, B., see Barrière, A.S. 600 Moncton, D.E., see Bohr, J. 30, 54 Moncton, D.E., see Gibbs, D. 6, 10, 13, 16 Monerie, M., see Allain, J.Y. 587, 591, 592 Monerie, M., see Ronarc'h, D. 588, 589 Mongorgé, R., see Benyattou, T. 596 Monochar, A., see Malik, S.K. 174, 175 Monod, P., see Caudron, R. 10 Moon, R.M., see Suzuki, H. 401, 413 Mooradian, A., see Zayhowski, J.J. 567, 599 Moore, C.E. 609, 682 Moos, H.W., see Riseberg, L.A. 548 Moos, H.W., see Wright, J.C. 346 Morariu, M. 202, 203, 205 Morariu, M., see Rogalski, M.S. 202, 205 Moreau, J.M., see Le Roy, J. 263 Morey, W.W., see Ball, G.A. 600 Morgan, M.J., see Bingham, D. 458, 459, 467 Mori, K., see Ishigaki, T. 318, 323 Mori, Y., see Sun, H. 258, 259 Morin, D., see Auzel, F. 578, 599 Morin, D., see Michel, J.C. 575 Morin, D., see Santa-Cruz, P.A. 578, 599 Morin, P. 301, 359 Morokhivskii, B.S., see Koterlin, M.D. 167, 174, 181, 182 Morokuma, K., see Hosoya, H. 611 Morokuma, K., see Ohta, K. 643 Morra, R.M. 428 Morris, D.E., see Zhang, H. 413, 421 Morris, I.D., see Bleaney, B. 318, 322, 351, 366, 367, 387 Morris Jr, J., see Khachaturyan, A.G. 473 Morrish, A.H., see Li, Z.W. 218, 219, 222 Morrison, C.A. 301, 312, 314 Morss, L.R. 305 Moruzzi, V.L., see Malozemoff, A.P. 149, 259 Moruzzi, V.L., see Williams, A.R. 259 Moskalev, V.N., see Dervagin, A.V. 270 Moskovits, M., see Kirkwood, A.D. 681 Moss, S.C., see Fontaine, D. 473 Mössbauer, R.L., see Barnes, R.G. 318, 323 Moutonnet, D., see Barrière, A.S. 600 Moutonnet, D., see Favennec, P.N. 597 Moutonnet, D., see Rolland, A. 595, 596

Moze, O. 157, 165, 167, 168, 176, 209, 210, 215, 228, 248, 272 Moze, O., see Li, H.-S. 215, 248 Moze, O., see Solzi, M. 156, 215, 216, 228, 243-246 Mroczkowski, S., see Folinsbee, J.T. 346, 428 Mroczkowski, S., see Ellingsen, O.S. 346, 413, 417 Mueller, R.M., see Folle, H.R. 400 Mueller, R.M., see Kubota, M. 400 Mukhamedshin, I.R., see Ishigaki, T. 318, 323 Mukhamedshin, I.R., see Teplov, M.A. 487, 489 Mukhin, A.A., see Kolmakova, N.P. 413 Mukhin, S.I., see Baak, J. 489 Müller, A. 146, 147 Muller, A.U. 419 Müller, G. 578 Müller, H.D., see Ennen, H. 594, 595 Muller, J., see Graf, T. 472, 473, 483, 490 Muller, J., see Sanchez, D. 490 Müller, K.A., see Bednorz, J.G. 478 Müller, K.A., see Deutscher, G. 478 Muller, K.A., see D'Iorio, M. 365 Muller, P., see Kleiner, R.K. 478 Muller, P.H. 319, 322, 405 Müller-Vogt, G., see Claus, H. 478 Müller-Vogt, G., see Riedling, S. 478 Müller-Westerhoff, U., see Streitwieser, A. 689 Murad, E. 660, 673, 674 Murad, E., see Dulick, M. 660-662, 666, 667, 669-674, 676 Murao, T. 401, 413, 414 Murasik, A., see Piotrowski, M. 305 Muroi, M. 478 Mutka, H., see Allenspach, P. 479 Mutka, H., see Guillaume, M. 318, 323 Mutka, H., see Mesot, J. 323, 475, 478 Mutscheller, W. 329 Mydlarz, T., see Baran, A. 148, 152-154, 163, 165, 167, 177, 178, 181, 188-190, 194, 195, 267, 268, 271, 273 Mydlarz, T., see Berezyuk, D.A. 237 Mydlarz, T., see Suski, W. 148, 154, 155, 168, 181, 183-185, 189, 191, 197, 267, 268, 271, 272, 277-279, 281, 283 Mydosh, J.A., see Dirkmaat, A.J. 459, 469-471 Myers, C.E. 610, 651, 685, 687 Naberhuis, S.L., see Fong, F.K. 548 Nafis, S., see Sellmyer, D.J. 87, 88 Nafis, S., see Shan, Z.S. 107 Nagai, H., see Amako, Y. 158-160 Nagai, H., see Deportes, J. 145 Nagai, H., see Okamoto, N. 145, 149, 158-160

Nagamine, L.C.C.M. 251 Nagase, S. 699, 700, 717 Nagase, S., see Kobayashi, K. 718 Nagele, W., see Gehring, G.A. 346, 413, 417, 419 Nakagawa, Y., see Kaneko, T. 209, 215 Nakagome, H. 597 Nakahara, S., see Hellman, F. 119 Nakajima, T. 413 Nakamura, H., see Wada, H. 168 Nakamura, Y., see Wada, H. 168 Nakazawa, E. 511, 556 Nakazawa, M. 599 Nakotte, H., see Andreev, A.V. 154, 202 Naletov, V.V., see Aminov, L.K. 441, 445, 448, 452, 454, 455 Naletov, V.V., see Bakharev, O.N. 472, 479, 481-483, 486-491 Naletov, V.V., see Teplov, M.A. 479, 487, 489 Nambudripad, N., see Allsop, A.L. 401 Nambudripad, N., see Suzuki, H. 400, 401 Namikura, Y., see Wakabayashi, H. 587 Narasinahan, P.T., see Sen, K.D. 317 Narayanan, K.S., see MacIsaac, A.B. 421 Nassau, K., see Johnson, L.F. 510 Natadze, A.L., see Kupchikov, A.K. 338, 404 Navarathna, A. 160 Navarathna, A., see Cadieu, F.J. 215, 264 Navarathna, A., see Hegde, H. 146, 160, 161 Nawate, M., see Honda, S. 90 Nawte, M., see Honda, S. 101 Naydyuk, Yu.G. 151, 181, 183, 189 Nazareth, A.S., see Fernando, A.S. 215, 228, 232, 258 Néel, M.L. 85 Neigaus, M.G., see Aleksandrov, I.V. 435 Neiva, A.C. 146, 147 Nejlo, G.N. 390 Neogy, A., see Neogy, D. 323 Neogy, D. 323 Neogy, D., see Sen, H. 319 Nessler, W., see Welp, U. 475 Neuhausen, S., see Braunisch, W. 478 Neumann, C.-S. 692 Neumann, C.-S., see Dolg, M. 629, 647, 654, 655, 692, 693, 716 Neuroth, N., see Müller, G. 578 Nevald, R. 443 Nevald, R., see Hansen, P.E. 443 Newman, D.J. 312, 313 Newman, D.J., see Bradbury, M.I. 313 Newman, D.J., see Chan, K.S. 338 Ng, B., see Newman, D.J. 312 Ni, H. 561, 562 Ni, J., see Li, Z. 610, 705

758

Niarchos, D., see Anagnostou, M.S. 263 Niarchos, D., see Christides, C. 209, 215, 228, 234, 237, 248-250, 253, 259, 261, 273 Nicklow, R.M., see Suzuki, H. 401, 413 Nicolaides, G.K., see Jurczyk, M. 222, 228-231, 233, 247, 248, 252 Nicolaides, G.K., see Yang, F.-M. 232, 233, 248, 249 Nicolay, K., see Bonrath, H. 413 Niedźwiedź, K., see Suski, W. 150, 268, 272, 279 Niemeijer, Th. 408 Nieuwenhuys, G.J., see Dirkmaat, A.J. 459, 469-471 Nieuwpoort, W.C. 635, 636 Nieuwpoort, W.C., see Aerts, P.J.C. 635 Nieuwpoort, W.C., see DeJong, W.A. 635, 707 Nieuwpoort, W.C., see Visscher, L. 613, 635, 708 Nieuwpoort, W.C., see Visser, O. 613, 614, 631, 632, 706-710, 712, 716 Nikitin, S.A., see Zolotukhin, O.A. 218 Nilsson, J., see Blixt, P. 593 Ning, T., see Hu, J. 237, 248 Nishida, N., see Ishimoto, H. 400 Nishihara, H., see Haruna, M. 599 Noakes, D.R., see Graham, J.T. 459 Nomura, T., see Amako, Y. 158, 159 Nordland, W.A., see Cohen, E. 365 Norman, L.J., see Myers, C.E. 610, 685 Norrington, P.H., see Grant, I.P. 612, 634 Notrys, H., see Egami, T. 94 Novak, P., see Kazei, Z.A. 301, 413 Nowak, B., see Suski, W. 150, 268, 272, 279 Nowicki, L.J., see Jorgensen, J.D. 475, 478 Nowik, I. 148, 154 Nowik, I., see Felner, I. 148, 163, 165, 167-169, 174, 175, 178, 181, 182, 185-188, 190, 191, 194-201 Nugteren, P.R., see Mennenga, G. 458, 468, 469 Nusair, M., see Vosko, S.H. 641, 659, 667, 680, 715 Nuttall, R.H.D., see Shin, S.C. 90 Oberg, M.G., see Van der Ziel, J.P. 597 O'Brien, S.C., see Kroto, H.W. 695 O'Brien, S.C., see Zhang, Q.L. 696 O'Brien, T., see Yafet, Y. 7, 50, 69 Ocio, M., see Hammann, J. 413 Odriozola, J.A., see Márquez, A. 665, 716 Oetliker, U. 561 Ogden, J.S., see Beattie, I.R. 686, 687 O'Grady, K. 126-128 Oguma, M., see Hattori, K. 599 Ogura, I., see Amako, Y. 158, 159 Oguro, I., see Andreev, A.V. 247, 275, 276

Ohashi, K. 148, 157, 209, 215, 216, 218, 219, 221, 228, 232, 233, 237 Ohashi, K., see Kaneko, T. 209, 215 Ohno, K., see Hosoya, H. 611 Ohno, T., see Guo, T. 696 Ohta, K. 643 Ohta, N., see Suzuki, Y. 119 Ohtsu, M., see Honda, S. 93 Ohtsuka, T., see Suzuki, H. 382, 400, 401, 413 Ohwaki, J., see Wang, Y. 599 Okada, K., see Kobayashi, H. 610, 700, 701 Okada, M. 209, 228, 232, 233, 237 Okamoto, N. 145, 149, 158-160 Oleś, A., see Bourée-Vigneron, F. 150, 152, 163, 165, 167-169 Olskansky, R. 587 Olsson, N., see Becker, P.C. 511, 537, 580, 588 Omori, Y., see Kitagawa, T. 599 Ono, K., see Ishimoto, H. 400 Ono, M., see Suzuki, H. 401 Opiła, J., see Baran, A. 267, 268, 271, 273 Oppenheimer, J.R., see Born, M. 629 Orbach, R. 552 Orbach, R., see Powell, M.J.D. 318, 323, 406 Oreg, J., see Malli, G.L. 635 Orendaneva, A., see Anders, A.G. 408 O'Riely, J., see Bulman, J.B. 413 Ortiz, J.V. 610, 689, 690 Osborn, R. 484 Osborn, R., see Guillaume, M. 318, 323 Osborn, R., see Mesot, J. 323 Osborn, R., see Podlesnyak, A. 318 O'Shea, M.J. 125 O'Shea, M.J., see Perera, P. 106, 108 O'Shea, M.J., see Sellmyer, D.J. - 88 Osofsky, M.S. 478 Ostrowsky, D.B., see Lallier, E. 599 Ostrowsky, D.B., see Li, M.J. 580, 599 Osugi, R., see Kaneko, T. 209, 215 Osugi, R., see Ohashi, K. 148, 157, 209, 215, 218, 219, 221, 228, 232, 237 Otani, Y. 265 Otani, Y., see Sun, H. 265 Ottschofski, E. 636 Ottschofski, E., see Kutzelnigg, W. 636 Overhauser, A., see Dick, B.G. 317 Ovsyankin, V.V. 511, 556-559 Owers-Bradley, J.R., see Kubota, M. 400 Pacios, L.F. 646 Pacios, L.F., see Hurley, M.M. 646 Padalia, B.D., see Darshan, B. 174, 175 Padalia, B.D., see Malik, S.K. 174, 175 Page, J.H. 427, 428

Page, J.H., see Graham, J.T. 459 Page, J.H., see Taylor, D.R. 459 Pagés, M., see Halevy, I. 186-189, 202 Païdassi, S., see Cochet-Muchy, D. 265 Paixão, J.A. 177, 178, 202, 286 Palacias, E., see Tomey, E. 237 Palacios, E., see Garcia, L.M. 237-239, 246, 247, 252 Palacios, E., see Luis, F. 237, 238, 252 Palenzona, A., see Iandelli, A. 145, 160, 161 Pan, D.K., see Wang, S.G. 613, 641, 660, 665, 667, 672, 675, 716 Pan, Q., see Ge, S.-L. 209, 215 Pan, Q., see Yang, Y.-C. 237, 261, 263 Pan, S.M., see Ma, R.H. 209, 228, 247 Pang, Y., see Grünberg, P. 39 Pappalardo, R., see Jørgensen, C.K. 313, 651 Papuchon, M., see Lallier, E. 599 Papuchon, M., see Li, M.J. 580, 599 Pareti, L. 228, 229, 232, 244, 245, 248 Pareti, L., see Li, H.-S. 215, 248 Pareti, L., see Moze, O. 215, 228, 248 Pareti, L., see Solzi, M. 156, 207, 209, 210, 215, 216, 218, 221, 228, 243-247 Pari, P., see Radhakrishna, P. 304, 413, 419 Park, B. 37 Park, B.J., see Everitt, B.A. 10, 14, 25, 65 Park, B.J., see Tsui, F. 35, 36 Park, C. 689 Parkin, S.S.P. 39, 48 Parkin, S.S.P., see Beyers, R. 474, 475 Parkin, S.S.P., see Falicov, L.M. 20, 32, 35, 47 Parkin, S.S.P., see Farrow, R.F.C. 21 Parpia, F.A., see Dyall, K.G. 612, 623, 624, 634, 655 Parpia, F.A., see Wijesundera, W.P. 623 Parrinello, M., see Car, R. 699 Parrinello, M., see Laasonen, K. 699 Partridge, H., see Dyall, K.G. 635 Paschenko, V.A., see Khat'sko, E.N. 413 Pashmakov, B., see Mogilevsky, R. 489 Pask, H.M., see Lauder, R.D.T. 590 Pasman, J.H.T., see Bleaney, B. 363, 364, 372, 373 Pastushkova, M.A., see Sokolovskaya, E.M. 157 Patterson, B.M., see Fernando, A.S. 215, 228, 232, 258 Patterson, G., see Mansuripur, M. 132 Paul, W., see Mensinger, H. 413, 419 Paulikas, A.P., see Jorgensen, J.D. 471, 475, 476, 478, 488 Paulikas, A.P., see Veal, B.W. 475, 478, 488 Paulikas, A.P., see Yang, S. 478 Pautrat, C., see Deutschbein, O.K. 510

Pavlidou, C.M.E., see Stoll, H. 641, 659, 667, 680 Pawlak, L., see Drulis, M. 181, 183 Payne, D.N., see Hewak, D.W. 599 Payne, D.N., see Mears, R.J. 580, 587, 591 Payne, D.N., see Reekie, L. 587 Payne, S.A., see De Loach, L.D. 549 Pearson, W.B. 152 Pechersky, V.K., see Gladyshevsky, E.I. 146-148, 154, 156, 206 Pécile, D., see Auzel, F. 550, 578, 599 Peck Jr, W.F., see Cava, R.J. 474, 475 Pei, Shiyou, see Jorgensen, J.D. 471, 476, 482, 488 Peierls, R.F., see Sternheimer, R.M. 314 Pekker, S. 472, 475, 479, 480, 483 Pekker, S., see Heinmaa, I. 475 Pekker, S., see Rockenbauer, A. 472, 475, 479, 480, 483 Pekurovskii, V.R. 322, 324, 352, 357 Pekurovskii, V.R., see Aminov, L.K. 300, 397, 399, 461, 469 Pekurovskii, V.R., see Malkin, B.Z. 352, 460, 470 Pekurovskii, V.R., see Vinokurov, A.V. 322, 338, 339 Pelenc, D. 600 Pelenc, D., see Chartier, I. 600 Pelenc, D., see Sheperd, D.P. 600 Pélissier, M., see Barthelat, J.C. 640, 646 Pélissier, M., see Chang, C. 638 Pélissier, M., see Teichteil, C. 648 Pellé, F. 559 Pellé, F., see Auzel, F. 559, 593 Pelletier, E., see Lallier, E. 599 Pelletier, R., see Pelletier-Allard, N. 562 Pelletier-Allard, N. 562 Peng, J.L., see Clinton, T.W. 422 Penneman, R.A., see Thoma, R.E. 302 Penney, W.G. 364 Pepper, M. 609, 613, 691 Percival, R.M. 590 Perdew, J.P. 681, 682, 700 Pereda, J.A., see Gal, J. 150, 154, 174, 176-178, 185, 201 Perera, P. 106, 108 Perrone, A., see Cosmovici, C.B. 673, 674 Perry, A.M., see Harley, R.T. 365, 458, 467 Petasis, D.T. 346, 413, 428 Peterson, G.E. 567 Peterson, M.A., see DeKock, R.L. 684, 688, 716 Petrov, V.M., see Krasnov, K.S. 686 Petrova, I.P., see Al'tshuler, S.A. 354, 434, 435 Pettit, G.D., see Sorokin, P.R. 510 Petzel, T. 687

760

Petzow, G., see Neiva, A.C. 146, 147 Peyerimhoff, S.D., see Von Arnim, M. 643 Pfeffer, J.Z., see Abraham, M.M. 445 Phillips, J.C. 477, 478, 642 Phillips, N.E. 490, 491 Phillips, N.E., see Emerson, J.P. 490 Phillips, N.E., see Hirvonen, M.T. 299, 413, 417 Phillips, N.E., see Katila, T.E. 413 Phillips, N.E., see Lee, W.C. 487 Piecuch, M., see Baczewski, C.T. 119 Piecuch, M., see Baudelet, F. 114 Piecuch, M., see Cherifi, K. 109-111 Piehler, D. 592 Pierce, D.T., see Falicov, L.M. 20, 32, 35, 47 Pigalskii, K.S., see Aleksandrov, I.V. 435 Pilawa, B. 312, 458, 459, 467 Pilawa, B., see Bischoff, H. 322 Pilawa, B., see Enderle, M. 318, 319 Pinchemel, B., see Carette, P. 666, 667 Pinkerton, F.E. 264 Pinot, M., see Bourée-Vigneron, F. 150, 152, 163, 165, 167-169 Pinto, H., see Gal, J. 163, 165, 177, 181, 182 Piotrowski, M. 305 Pisarenko, V.F., see Avanesov, A.G. 323, 324 Pittel, B., see Chang, T.-C. 644 Pittini, R., see Wachter, P. 490 Pitzer, K.S. 612, 646 Pitzer, K.S., see Bagus, P.S. 626, 627 Pitzer, K.S., see Balasubramanian, K. 612, 617 Pitzer, K.S., see Christiansen, P.A. 612, 613, 646, 648 Pitzer, K.S., see Lee, Y.S. 647 Pitzer, R.M. 645, 648 Pitzer, R.M., see Chang, A.H.H. 613, 648, 649, 658, 677, 691, 697, 698, 717 Pitzer, R.M., see Dolg, M. 629, 647, 648, 692-694, 716 Pitzer, R.M., see Kotzian, M. 648, 649 Pitzer, R.M., see Küchle, W. 625 Plackowski, T., see Suski, W. 272, 279, 280, 282, 283 Plaskett, T.S., see Mehran, F. 387, 391, 392, 398 Plugaru, N., see Burzo, E. 146, 202, 203, 205, 206 Plugaru, N., see Morariu, M. 202, 203, 205 Plugaru, N., see Rogalski, M.S. 202, 205 Plummer, E.P., see Dyall, K.G. 612, 623, 624, 634, 655 Poate, J.M., see Adler, D.L. 598 Poate, J.M., see Schubert, E.F. 600 Pobell, F. 400 Pobell, F., see Folle, H.R. 400 Pobell, F., see Kubota, M. 400

Pocholle, J.P., see Lallier, E. 599 Pocholle, J.P., see Li, M.J. 580, 599 Podlesnyak, A. 318 Poignant, H., see Allain, J.Y. 587, 591, 592 Poignant, H., see Auzel, F. 586, 588 Poignant, H., see Ronarc'h, D. 537, 588, 589 Poindexter, J.M., see Barnes, R.G. 318, 323 Poirier, M., see Vial, J.C. 559 Polder, D. 526, 531 Polder, D., see Schuurmans, M.F.H. 529, 532, 537 Polman, A. 599 Pominov, A.I., see Vinokurov, A.V. 322, 338, 339 Pommier, J. 404 Pomrenke, G.S. 599 Pomrenke, G.S., see Ennen, H. 594 Poole, S.B., see Mears, R.J. 580, 587, 591 Poole, S.B., see Reekie, L. 587 Pop, J., see Coldea, R. 167, 168 Popenko, N.I. 686 Popenko, N.I., see Krasnov, K.S. 686 Popiel, E.S. 194, 195 Pople, J.A. 649, 704 Popma, T.J.A., see Horst, F. 600 Popov, Yu.F., see Vekhter, B.G. 361 Porté, B., see Barrière, A.S. 600 Potopowicz, J.R., see Singh, S. 538, 575 Potter, J.F., see MacChesney, J.B. 413 Potzel, W., see Gal, J. 150, 154, 163, 165, 176-178, 181, 182, 185, 201 Potzel, W., see Halevy, I. 186-189, 202 Poulain, M., see Auzel, F. 588 Pound, R.V., see Bloembergen, N. 379 Pouradier, J.F. 551, 552 Pouzet, C., see Aleonard, S. 305 Powell, M.J.D. 318, 323, 406 Powers, J.M., see Ross, R.B. 646 Prabhawalkar, P.D., see Malik, S.K. 174, 175 Preuß, H. 644 Preuß, H., see Andrae, D. 647 Preuß, H., see Bergner, A. 647 Preuß, H., see Dolg, M. 613, 618-620, 625, 628, 629, 640, 647, 648, 651, 653-655, 657-661, 663-666, 668-670, 672-677, 679-682, 686-688, 692-694, 716 Preuß, H., see Fuentealba, P. 647 Preuß, H., see Igel-Mann, G. 647 Preuß, H., see Küchle, W. 613, 618, 619, 640, 647, 670 Preuß, H., see Stoll, H. 641, 659, 667, 680 Prewitt, C.T., see Shannon, R.D. 624 Primakoff, H., see Holstein, T. 408 Prinz, G., see Falicov, L.M. 20, 32, 35, 47 Projevudsky, A.K., see Kustov, E.F. 572 Prokhorov, A.D., see Krygin, I.M. 456

Prokhorov, A.D., see Nejlo, G.N. 390 Prokhorov, A.M., see Vagin, Y.S. 549 Pshisukha, A.M. 413 Ptasiewicz-B,ak, B. 150, 176, 177, 181-183, 190, 194, 195 Ptasiewicz-B.ak, B., see Piotrowski, M. 305 Pukhov, K.K., see Aleksandrov, I.V. 435 Purcell, E.M., see Bloembergen, N. 379 Puri, S.P., see Vishwamittar, X. 302 Purwins, H.G. 301 Pyper, N.C. 643 Pyper, N.C., see Grant, I.P. 612, 634 Pyper, N.C., see Malli, G.L. 635 Pyper, N.C., see Rose, S.J. 617, 643 Pytte, E., see Aharony, A. 36, 70 Pyykkö, P. 609-614, 617-622, 625, 626, 632, 634, 650, 655, 684, 685 Pyykkö, P., see Desclaux, J.P. 634 Pyykkö, P., see Hotokka, M. 682 Pyykkö, P., see Larsson, S. 650 Pyykkö, P., see Lohr, L.L. 613, 650 Pyykkö, P., see Marian, C.M. 670 Pyykkö, P., see Snijders, J.G. 617, 619 Qi, Q.-N. 263 Qian, C., see Li, J. 610 Quezel, G. 413 Quezel, G., see Abbas, Y. 413, 418 Quezel, G., see Ballestracci, R. 418 Quezel, G., see Rossat-Mignod, J. 413, 418 Quezel-Ambrunaz, S., see Kappatsch, A. 413 Quimby, R.S. 593 Quiney, H.M. 635 Quiney, H.M., see Grant, I.P. 612, 634 Rabaâ, H. 610, 703 Rable, K.M., see Cava, R.J. 474, 475 Racah, G. 634 Rachford, F.J. 390, 392 Racz, Z., see Xu, H.-J. 418 Radaelli, P.G., see Jorgensen, J.D. 482 Radhakrishna, P. 304, 413, 419 Radousky, H.B., see Rosov, N. 413 Radtke, D.D., see DeKock, C.W. 686, 687 Radwański, R.J., see Verhoef, R. 135 Radzig, A.A. 612 Raevskaya, M.V., see Sokolovskaya, E.M. 157 Rai, D.K., see Yadav, B.R. 666 Rai, S.B., see Yaday, B.R. 666 Rajagopal, A.K., see Ramana, M.V. 613, 641 Rakavy, M., see Felner, I. 190, 194-197 Rakhmatullin, R.M., see Antipin, A.A. 382, 384, 385, 390, 392, 393 Ramana, M.V. 613, 641

Rameix, A., see Sheperd, D.P. 600 Ramey, J.O., see Rappaz, M. 392 Ramirez, M.L., see Beyers, R. 474, 475 Rancurel, P., see Huron, B. 648 Rand, S.C., see Ni, H. 561, 562 Rani, R., see Cadieu, F.J. 215, 264 Rani, R., see Hegde, H. 146, 160, 161 Rani, R., see Navarathna, A. 160 Rao, K.V., see Jurczyk, M. 222, 228-231, 233, 240, 241, 247, 248, 252 Rao, K.V., see Yang, F.-M. 232, 233, 248, 249 Raoux, S., see Barrière, A.S. 600 Rappaz, M. 392 Rappé, A.K. 646 Ratajczak, H., see Beznosov, A.B. 150, 273 Ratajczak, H., see Lunkenheimer, P. 185 Rath, J. 258 Rauchschwalbe, U. 178, 181-183, 195 Rauh, E.G., see Ackermann, R.J. 651, 666 Ravenek, W., see Ziegler, T. 684, 688 Ravenhall, D.G., see Brown, G.E. 636 Razgonyaev, S.M., see Andreev, A.V. 148, 215, 248 Réan, M., see Barrière, A.S. 600 Rebelsky, L. 272 Rechenberg, H.R., see Nagamine, L.C.C.M. 251 Redfield, A.G. 379 Reedy, G.T., see Gabelnick, S.D. 670, 671, 673, 684 Reekie, L. 587 Reekie, L., see Mears, R.J. 580, 587, 591 Regev, D., see Gal, J. 150, 154, 176-178, 185, 201 Regev, D., see Halevy, I. 186-189, 202 Reich, D.H. 458, 469-471 Reich, D.H., see Rosenbaum, T.F. 458 Reid, M.P., see Richardson, F.S. 318 Reihardt, W., see Schweiss, P. 484 Reim, W., see Brände, H. 150, 270 Reimer, P.M. 16 Reimer, V.A., see Kudrevatykh, N.V. 249 Reisfeld, R. 510 Ren, J. 610, 613, 649, 705 Ren, J., see Huang, L. 705 Ren, J., see Li, J. 610, 695 Ren, J., see Li, L. 610, 613, 649, 685, 706 Ren, J., see Li, Z. 610, 705 Ren, J., see Xu, G. 610, 649, 703, 705 Ren, Y.G., see Jaswal, S.S. 254-256 Ren, Y.G., see Zhao, Z.R. 265 Renard, J.P., see Beauvillain, P. 321, 346, 413, 420, 424, 425, 468 Renard, J.P., see Mennenga, G. 458, 468, 469 Reyes, O., see Fuentealba, P. 647

Reyes-Gasga, J. 474, 475, 478 Reza, K.A. 459, 468 Reznik, D., see Cooper, S.L. 477 Rhyne, J.J. 10, 14, 46, 48, 49, 51, 52, 61 Rhyne, J.J., see Beach, R.S. 21, 22, 24, 25, 30, 45, 46, 59, 62 Rhyne, J.J., see Borchers, J.A. 11, 24, 30, 42, 46, 55, 57 Rhyne, J.J., see Erwin, R.W. 40, 41, 44, 46, 48, 52, 54 Rhyne, J.J., see Everitt, B.A. 25, 65 Rhyne, J.J., see Flynn, C.P. 47, 66 Rhyne, J.J., see Salamon, M.B. 3, 14, 21, 39, 46, 48, 52, 70 Rhyne, J.J., see Tsui, F. 65, 66, 68 Rhys, A., see Huang, K. 547 Rice, S., see Linton, C. 672-674 Rice, S.A., see Hazi, A.U. 642 Rice, S.A., see Weeks, J.D. 646 Rice, S.F., see McDonald, S.A. 651, 673, 675 Rice, T.M., see Sigrist, M. 478 Richardson, F.S. 318 Riedling, S. 478 Riedling, S., see Claus, H. 478 Rietschel, H., see Schreiner, Th. 489 Rigsbee, J.T., see Streitwieser, A. 610, 689, 691 Riley, M.J., see Oetliker, U. 561 Rimai, L. 387, 392 Rinaldi, S., see Asti, G. 243 Rios Leite, J.R. 557 Riseberg, L.A. 365, 548 Riseberg, L.A., see Cohen, E. 365 Risk, W.P., see Tong, F. 591 Riski, K.J., see Hirvonen, M.T. 299, 413, 417 Ritley, K., see Reimer, P.M. 16 Rittner, E.S. 614 Robertson, I.L., see Dixon, R.N. 646 Robinson, C., see Egami, T. 94 Robinson, F.N.H., see Bleaney, B. 363, 366, 368, 373 Robinson, M., see Asawa, C.K. 567 Robinson, M.G., see Baker, J.M. 391, 444 Robinson, M.G., see Bleaney, B. 366, 367 Robinson, N.H.F., see Kurti, N. 399 Rochaix, C. 594 Rochaix, C., see Rolland, A. 595, 596 Roche, K.P., see Beyers, R. 474, 475 Rockenbauer, A. 472, 475, 479, 480, 483 Rockenbauer, A., see Pekker, S. 472, 475, 479, 480, 483 Roden, B., see Braunisch, W. 478 Rodionova, M.P., see Bakharev, O.N. 318, 323, 479 Rodionova, M.P., see Eremin, M.V. 325

Roess, D. 510, 540 Roessli, B. 413 Roessli, B., see Guillaume, M. 473 Rogacki, K., see Suski, W. 272, 279, 280, 282, 283 Rogalski, M.S. 202, 205 Rogalski, M.S., see Morariu, M. 202, 203, 205 Rogl, P., see Weitzer, F. 146, 202, 203, 205, 206 Röhberg, K., see Claus, H. 478 Rohberg, K., see Riedling, S. 478 Rohrer, H. 468 Roinel, Y. 386 Roinel, Y., see Bleaney, B. 401 Rojo, A.G., see Aligia, A.A. 473 Rolland, A. 595, 596 Rolland, A., see Rochaix, C. 594 Ronarc'h, D. 537, 588, 589, 593 Ronarc'h, D., see Clescla, B. 588 Roos, B.O., see Hotokka, M. 682 Roothaan, C.C.J. 635 Ros, P., see Snijders, J.G. 641, 659, 667, 680 Rösch, N. 610, 629, 638, 641, 650, 689-691, 696, 697, 716 Rösch, N., see Cory, M.G. 614, 649 Rösch, N., see Culberson, J.C. 610, 613, 649, 685, 686, 688, 703 Rösch, N., see Dunlap, B.I. 641, 696 Rösch, N., see Häberlen, O.D. 638, 641, 696, 716 Rösch, N., see Jahns, V. 649, 703, 717 Rösch, N., see Knappe, P. 696 Rösch, N., see Kotzian, M. 613, 648, 649, 663, 665, 666, 668, 669, 676, 701, 702, 717 Rösch, N., see Streitwieser, A. 610, 689, 691 Rösch, N., see Thornton, G. 641 Rose, S.J. 617, 643 Rosén, A. 641, 697, 698, 700, 716 Rosén, A., see Lindgren, I. 612, 634 Rosen, M. 14, 59 Rosenbaum, T.F. 458 Rosenbaum, T.F., see Reich, D.H. 458, 469-471 Rosenbaum, T.F., see Wu, W. 458, 469 Rosenberg, H.M., see Metcalfe, M.J. 413 Rosenberg, M., see Ding, J. 209, 218, 228, 265 Rosenberg, M., see Sinnemann, Th. 209, 215, 228, 241 Roser, M.R. 408, 413, 417 Roser, M.R., see Corruccini, L.R. 413 Roser, M.R., see Xu, J. 413 Rosicky, F. 635 Rosicky, F., see Mark, F. 635 Rosov, N. 413 Ross, R.B. 613, 646, 654, 655 Ross, R.B., see Ermler, W.C. 612, 613, 646 Ross, R.B., see Hurley, M.M. 646

Ross, R.B., see LaJohn, L.A. 646 Rossat-Mignod, J. 413, 418 Rossat-Mignod, J., see Abbas, Y. 413, 418 Rossat-Mignod, J., see Filippi, J. 413 Rossat-Mignod, J., see Quezel, G. 413 Rossat-Mignod, J., see Tolentino, H. 486 Rothman, S.J. 475 Rotter, M., see Zeleny, M. 162, 200, 267, 268, 273 Rousseau, M., see Cozannet, A. 582 Routbort, J.L., see Rothman, S.J. 475 Rüegg, S., see Schütz, G. 140 Ruhle, M., see Mayer, J. 16 Rundle, R.E., see Fitzwater, D.R. 301 Rundle, R.E., see Florio, J.V. 145 Rupp Jr, L.W., see Cava, R.J. 474, 475 Ruščić, B. 610, 641, 685, 686 Rushworth, A.J., see Glynn, T.J. 365 Rutkowski, A. 636 Rutkowski, A., see Jankowski, K. 636 Ryan, D.H., see Liao, L.X. 261 Ryan, J.F., see Bleaney, B. 363, 366 Rykhal, R.M., see Zarechnyuk, O.S. 146, 147 Ryskin, A.I., see Kupchikov, A.K. 318, 321, 338, 404 Rzaev, D.A., see Kupchikov, A.K. 318, 321 Sachs, L.M., see Kaufman, J.J. 682 Sadoc, A., see Santa-Cruz, P.A. 578, 599 Safiullin, A.R., see Aminov, L.K. 441, 445, 448, 452, 454, 455 Sahashi, M., see Sakurada, S. 146, 207, 209 Saillard, J.-Y., see Rabaâ, H. 610, 703 Saito, H. 265 Sakai, Y. 639, 644 Sakatsume, S., see Suzuki, H. 401 Sakhaeva, S.I., see Aminov, L.K. 300, 388, 390, 392, 393, 396, 397, 399, 461, 469 Sakharov, V.A. 425 Sakuma, A. 257, 258 Sakurada, S. 146, 207, 209 Sakurai, J., see Ohashi, K. 157, 215, 218, 221 Salahub, D.R. 612 Salamon, M.B. 3, 14, 21, 39, 46, 48, 52, 70 Salamon, M.B., see Beach, R.S. 21, 22, 24, 25, 30, 45, 46, 57, 59, 62 Salamon, M.B., see Borchers, J.A. 11, 24, 30, 42, 46, 55, 57, 58 Salamon, M.B., see Erwin, R.W. 40, 41, 44, 46, 48, 52, 54 Salamon, M.B., see Everitt, B.A. 10, 14, 25, 65 Salamon, M.B., see Falicov, L.M. 20, 32, 35, 47 Salamon, M.B., see Flynn, C.P. 47, 66 Salamon, M.B., see Rhyne, J.J. 46, 48, 49, 51, 52

Salamon, M.B., see Tanaka, Y. 25, 30, 31 Salamon, M.B., see Tsui, F. 66, 68 Salem, J., see Johnson, R.D. 699 Salikhov, I.Kh., see Aminov, L.K. 300, 388, 390, 392, 393, 396, 397 Salikhov, I.Kh., see Eremin, M.V. 325 Salikhov, I.Kh., see Kurkin, I.N. 475 Salje, E.K.H., see Chrosch, J. 474, 475 Salpeter, E.E., see Bethe, H.A. 629 Salvi, M., see Favennec, P.N. 594, 597 Salvi, M., see Rochaix, C. 594 Samant, M.G., see Wu, Y. 125 Samelson, H., see Lempicki, A. 510 Samhoun, K., see David, F. 624 Samson, B.N., see Hewak, D.W. 599 Samzow, R. 637 Sanchez, D. 490 Sankar, S.G., see Cheng, S.F. 218 Sankar, S.G., see Sinha, V.K. 215, 216, 218, 219, 221, 222, 248 Santa-Cruz, P.A. 578, 599 Santa-Cruz, P.A., see Malta, O.L. 600 Santry, D.P., see Pople, J.A. 704 Sanz, J.F., see Márquez, A. 665, 716 Saroyan, R.A., see Stokowski, S.E. 575, 579 Saslow, W.M., see Chudnovsky, E.M. 70 Sato, N. 89-91, 94, 134 Sato, N., see Yamauchi, K. - 90 Satoh, M. 317 Saue, T., see Visscher, L. 613, 635, 708 Sauteret, C., see Gouedard, C. 538, 539 Saville, I.D., see Harley, R.T. 458, 467 Savin, A., see Dolg, M. 613, 619, 625, 628, 640, 647, 654, 655, 657, 660, 661, 677, 686-688, 716 Schaack, G., see Dahl, M. 338 Schaack, G., see Dorfler, W. 338 Schäfer, H., see Cordier, G. 181 Schäfer, W. 174, 176-178, 185 Schäfer, W., see Gal, J. 150, 154, 163, 165, 174, 176-178, 181, 182, 185, 201 Schäfer, W., see Halevy, I. 186-189, 202 Schäfer, W., see Kockelmann, W. 154, 185-188, 413 Schäfer, W., see Will, G. 304, 413, 419 Schafer-Siebert, D., see Kasten, A. 458, 459 Schäffer, C.E. 651 Schamps, J., see Dulick, M. 676 Scharenberg, W., see Will, G. 419 Schaub, B., see Frowein, R. 424 Schawlow, A.L., see Carlson, N.W. 536 Scherbakova, Ye.V. 237, 238, 248 Scherbakova, Ye.V., see Andreev, A.V. 284-286

Scherbakova, Yc.V., see Ermolenko, A.S. 154, 155, 207, 209, 233, 234, 237, 249, 250

Scheringer, C., see Lohmuller, G. 304 Schienle, M., see Muller, P.H. 319, 322, 405 Schiller, A. 532 Schinkmann, M., see Bonrath, H. 413 Schirber, J.E., see Vaknin, D. 479 Schlachetzki, A. 405 Schlaphot, W., see Enderle, M. 318 Schlapp, R., see Penney, W.G. 364 Schleger, P. 486 Schleyer, P.v.R., see Kaupp, M. 690, 716 Schloemann, E., see Leibfried, G. 577 Schlüter, M., see Bachelet, G.B. 646, 699 Schlüter, M., see Hamann, D.R. 646 Schmid, D., see Florian, R. 527, 532 Schmid, D., see Schiller, A. 532 Schmidt, G., see Lohmuller, G. 304 Schmidt, H., see Schreiner, Th. 489 Schmidt, P.G. 317, 324 Schmidt, V.H., see Jones, E.D. 363 Schmidtke, H.-H., see Jørgensen, C.K. 313, 651 Schmitt, D., see Morin, P. 301, 359 Schneider, J., see Ennen, H. 594 Schneider, J., see Kaufman, U. 595 Schnitzke, K. 266 Schnitzke, K., see Schultz, L. 265, 266 Schoenes, J., see Brände, H. 150, 270 Scholz, B. 109, 111, 112 Scholz, B., see Attenkofer, K. 114, 115 Scholz, B., see Badía, F. 110 Schopper, H.C., see Kahle, H.G. 413 Schreiber, R., see Grünberg, P. 39 Schreiner, Th. 489 Schröder, D., see Heinemann, C. 619, 620, 684, 716 Schrödinger, E. 629 Schtaudte, M., see Volodin, A.G. 386 Schtoyko, M.Yu., see Zarechnyuk, O.S. 146, 147 Schubert, E.F. 600 Schuchert, H., see Bonrath, H. 413 Schuller, I.K. 15 Schuller, I.K., see Dunlap, B.D. 413 Schuller, I.K., see Falicov, L.M. 20, 32, 35, 47 Schultz, L. 264-266 Schultz, L., see Katter, M. 265 Schultz, L., see Schnitzke, K. 266 Schuster, H., see Frowein, R. 424 Schütz, G. 140 Schütz, G., see Attenkofer, K. 114, 115 Schutzmann, J. 478 Schuurmans, M.F.H. 528, 529, 532, 537 Schuurmans, M.F.H., see Polder, D. 526, 531 Schwab, G. 392 Schwab, M., see Enderle, M. 319 Schwab, M., see Hulsing, H. 413, 418

Schwab, M., see Laugsch, J. 343, 346 Schwabe, H., see Volodin, A.G. 386 Schwabl, F., see Frey, E. 425 Schwan, L.O. 527, 528 Schwan, L.O., see Florian, R. 527, 532 Schwan, L.O., see Schiller, A. 532 Schwarz, H., see Heinemann, C. 619, 620, 684, 716 Schwarz, W.H.E. 615, 617, 620-622, 633, 635, 638, 643 Schwarz, W.H.E., see Baerends, E.J. 617 Schwarz, W.H.E., see Chang, T.-C. 643, 644 Schwarz, W.H.E., see Esser, M. 635, 648 Schwarz, W.H.E., see Hafner, P. 622, 643, 645, 648 Schwarz, W.H.E., see Mark, F. 635, 636 Schwarz, W.H.E., see Wang, S.G. 613, 620, 625, 626, 629, 641, 659, 660, 665, 667, 672, 675, 680, 716 Schwarzbauer, H.J., see Hulsing, H. 413, 418 Schweiss, P. 484 Schwerdtfeger, P. 682, 716 Schwerdtfeger, P., see Baerends, E.J. 617 Schwerdtfeger, P., see Eliav, E. 613, 627 Schwerdtfeger, P., see Seth, M. 626, 627, 647 Scott, B.P. 591 Scott, P.L. 393 Scuseria, G.E., see Guo, T. 696 Sechovsky, V. 148, 150, 272, 281 Sechovsky, V., see Andreev, A.V. 148, 215 Sedov, L.L., see Eremin, M.V. 325 Sedov, L.L., see Kurkin, I.N. 475 Seely, M.L., see Van Zee, R.J. 658, 679 Segal, G.A., see Pople, J.A. 704 Seghier, D. 596, 597 Seghier, D., see Benyattou, T. 596 Segre, C., see Dunlap, B.D. 413 Segre, C.U., see Jorgensen, J.D. 482 Seh, M., see Felner, I. 185-188, 190, 191, 194-197, 199 Seidel, B., see Suski, W. 185, 268, 272, 282, 283 Seidel, E.R., see Katila, T.E. 413 Seiden, J., see Beauvillain, P. 468 Seifert, C., see Hess, G. 459, 466, 467 Seijo, L. 644 Seijo, L., see Barandiarán, Z. 639, 644 Seijo, L., see Huzinaga, S. 644 Sellmann, D., see Kotzler, J. 405 Sellmyer, D.J. 87, 88, 140 Sellmyer, D.J., see Fernando, A.S. 215, 228, 232, 258 Sellmyer, D.J., see Jaswal, S.S. 254-256 Sellmyer, D.J., see Kirby, R.D. 83, 105, 125, 128-131

Sellmyer, D.J., see O'Shea, M.J. 125 Sellmyer, D.J., see Shan, Z.S. 84, 87, 90-93, 95-103, 105-107, 116-118, 121, 122, 124, 125, 134 Sellmyer, D.J., see Singleton, E.W. 263, 264 Sellmyer, D.J., see Zhang, H.Y. 91 Sellmyer, D.J., see Zhao, Z.R. 265 Semenkoff, M., see Clescla, B. 588 Semenova, E.A., see Krjukov, E.V. 479, 488, 489 Semenovskaya, S. 473, 474, 477 Sen. H. 319 Sen, K.D. 317 Sergeev, V.V., see Zolotukhin, O.A. 218 Sermage, B., see Lhomer, C. 596 Serota, R.A., see Chudnovsky, E.M. 70 Seth, M. 626, 627, 647 Sewai, H., see Haruna, M. 599 Shaheen, S.A., see Xu, Xie 237, 238 Shaked, H., see Gal, J. 163, 165, 177, 181, 182 Sham, L.J., see Kohn, W. 641, 700 Shami, G., see Gal, J. 150, 154, 176-178, 185, 201 Shan, Z.S. 84, 87, 90-93, 95-103, 105-107, 116-118, 121, 122, 124, 125, 134 Shan, Z.S., see Kirby, R.D. 128, 129 Shan, Z.S., see Kusov, A.A. 133 Shan, Z.S., see Zhang, H.Y. 91 Shannon, R.D. 624 Sharp, G.R., see Misra, S.K. 392 Shcherba, I.D. 151-153, 163, 165, 167, 168, 174, 175, 181, 182 Shcherba, I.D., see Koterlin, M.D. 167, 174, 181, 182 Shekhtman, V.Sh., see Bredikhin, S.I. 477 Shelby, R.M. 531 Shelby, R.M., see Macfarlane, R.M. 531 Shelton, R.N., see Clinton, T.W. 413, 422 Shelton, R.N., see Rosov, N. 413 Shen, B.G., see Cao, L. 215 Shen, H., see Sun, L. 477 Shen, J.X. 92, 94, 101-104 Shen, J.X., see Kirby, R.D. 83, 105, 125, 128-131 Shen, J.X., see Shan, Z.S. 91, 98, 99, 105, 116-118, 121, 122, 124 Shen, J.X., see Zhang, H.Y. 91 Sheperd, D.P. 600 Sheperd, D.P., see Chartier, I. 600 Sheperd, D.P., see Pelenc, D. 600 Sherwood, R.C., see Cohen, E. 365 Sherwood, R.C., see MacChesney, J.B. 413 Shi, H., see Jorgensen, J.D. 471, 476, 488 Shi, H., see Veal, B.W. 475, 478, 488 Shick, L.K., see Singh, S. 538, 575 Shiga, M., see Wada, H. 168

Shimao, M., see Ohashi, K. 148, 209, 215, 219, 228, 232, 237 Shimizu, M., see Kitagawa, T. 599 Shimoda, M., see Isago, H. 695 Shin, S.C. 90 Shing, Y.H., see Smith, M.R. 392 Shinjo, T., see Mibu, K. 90, 113, 114, 121 Shinjo, T., see Scholz, B. 109, 111, 112 Shinjo, T., see Yoden, K. 90, 112, 113 Shinohara, T., see Amako, Y. 158, 159 Shinomara, M., see Ishimoto, H. 400 Shionoya, S., see Nakazawa, E. 511, 556 Shionoya, S., see Yamada, N. 553 Shirane, G., see Birgeneau, R.J. 365 Shpak, A.P., see Shcherba, I.D. 151-153, 163, 165, 167, 168, 174, 175, 181, 182 Sibai, A.M., see Bernard, A. 661 Sibley, W.A., see Yeh, D.C. 593 Siddons, D.P., see Isaacs, E.D. 6, 10, 13, 16 Siegal, M., see Morss, L.R. 305 Sigaev, S.S., see Andreev, A.V. 148, 215, 221, 222, 245, 246, 248-250 Sigaev, S.S., see Kudrevatykh, N.V. 249 Sigmund, E., see Eremin, M.V. 490 Sigrist, M. 478 Silbernagel, B.G., see McHenry, M.R. 487 Silkin, N.I., see Zhdanov, R.Sh. 367 Silva, J.F.A., see Cooke, A.H. 413, 420 Silversmith, A.J., see Macfarlane, R.M. 591 Simas, A.M., see Andrade, A.V.M. 651, 704, 705, 717 Simizu, S. 413, 418, 458, 469 Simizu, S., see Bellesis, G.H. 413 Simizu, S., see Petasis, D.T. 346, 413, 428 Simkin, D.J., see Malcuit, M.S. 528, 532 Simon, A., see Gehring, G.A. 346, 413, 417, 419 Simon, F.E., see Kurti, N. 399 Simoni, E., see Brandel, V. 577 Simonov, V.I., see Voronkova, V.I. 475 Simons, D.S., see Salamon, M.B. 14 Simpson, J.A. 46, 65 Simpson, J.R., see Becker, P.C. 511, 537, 580, 588 Simpson, J.R., see Desurvire, E. 587 Simpson, J.R., see Giles, C.R. 587 Singh, S. 538, 575 Singleton, E.W. 263, 264 Singleton, E.W., see Strzeszewski, J. 263, 265 Singleton, E.W., see Zhao, Z.R. 265 Sinha, S., see Borchers, J.A. 46 Sinha, S., see Erwin, R.W. 40, 41, 44, 46, 48, 52 Sinha, S., see Rhyne, J.J. 46, 48 Sinha, S., see Salamon, M.B. 3, 14, 21, 39, 46, 48

Sinha, S.K., see Liu, S.H. 9 Sinha, V.K. 215, 216, 218, 219, 221, 222, 248 Sinha, V.K., see Cheng, S.F. 218 Sinha, V.K., see Zhang, L.Y. 248, 249 Sinnemann, Th. 209, 215, 228, 241 Sivardiere, J., see Kappatsch, A. 413 Skanthakumar, S. 413 Skelton, E.F., see Osofsky, M.S. 478 Skjeltorp, A.T. 346, 413 Skjeltorp, A.T., see Catanese, C.A. 343, 346, 413 Skieltorp, A.T., see Ellingsen, O.S. 346, 413, 417 Skolozdra, R.V., see Berezyuk, D.A. 148 Skovgaard, P.M.W., see Brorson, S.D. 600 Skrebnev, V.A., see Aukhadeev, F.L. 368, 377, 382 Skribanowitz, N. 525, 527, 535 Skvorchuk, V.P., see Bodak, O.I. 157 Slaski, M., see Dunlap, B.D. 413 Slater, J.C. 632 Smalley, R.E., see Chai, Y. 696, 699 Smalley, R.E., see Guo, T. 696 Smalley, R.E., see Kroto, H.W. 695 Smalley, R.E., see Zhang, Q.L. 696 Smart, R.G. 592 Smart, R.G., see Carter, J.N. 590 Smedley, T., see Rappé, A.K. 646 Smirnov, B.M., see Radzig, A.A. 612 Smit, H.H.A., see Buschow, K.H.J. 209, 210, 215, 228, 232, 237, 241, 269, 273 Smith, M.R. 392 Smith, R.D., see Richardson, F.S. 318 Smith, R.S., see Ennen, H. 594, 595 Smith, S.H., see Bleaney, B. 363, 368 Smith, S.R.P., see Elliott, R.J. 319, 329 Smith, S.R.P., see Graham, J.T. 459 Smith, S.R.P., see Harley, R.T. 365, 458, 467 Smith, S.R.P., see Page, J.H. 427, 428 Snijders, J.G. 617, 619, 641, 659, 667, 680 Sniiders, J.G., see Baerends, E.J. 617 Snijders, J.G., see Boerrigter, P.M. 691 Snijders, J.G., see Pyykkö, P. 619 Snijders, J.G., see Schwarz, W.H.E. 615, 617 Snijders, J.G., see Van Lenthe, E. 638 Snijders, J.G., see Ziegler, T. 619, 684, 688 Snitzer, E. 510, 556, 580, 586 Snoeks, E., see Polman, A. 599 Snow, A.I., see Florio, J.V. 145 Sobelman, I.I. 611 Soderholm, L., see Dunlap, B.D. 413 Soderholm, L., see Loong, C.-K. 318, 319, 321, 322 Sokolov, V.I. 350, 351, 459, 466-468 Sokolov, V.I., see Belov, K.P. 413

Sokolov, V.I., see Bondar', I.A. 355, 356, 359, 360 Sokolov, V.I., see Kazei, Z.A. 301, 413, 429 Sokolov, V.I., see Vasil'ev, A.V. 459, 466, 467 Sokolov, V.I., see Vekhter, B.G. 429 Sokolovskaya, E.M. 157 Solov'yanova, T.V., see Sokolov, V.I. 350, 351 Solzi, M. 156, 207, 209, 210, 215, 216, 218, 221, 228, 243-247 Solzi, M., see Moze, O. 215, 228, 248 Solzi, M., see Pareti, L. 228, 229, 232, 244, 245, 248 Sommerer, S.O., see Cundari, T.R. 704, 718 Somov, A.R., see Malkin, B.Z. 352, 460, 470 Sonntag, R., see Zeiske, T. 475 Sorel, Y., see Clescla, B. 588 Sorokin, P.R. 510 Sorokina, N.I., see Voronkova, V.I. 475 Soubeyroux, J.L., see Garcia, L.M. 237-239, 246, 247, 252 Soubeyroux, J.L., see Luis, F. 237, 238, 252 Soubeyroux, J.L., see Tomey, E. 237, 261 Soulem Jr, R.J., see Osofsky, M.S. 478 Sowers, H., see Gibbs, D. 13 Sowers, H., see Grünberg, P. 39 Sparn, G., see Geibel, C. 154, 183 Spiegelmann, F., see Teichteil, C. 648 Spijkerman, J., see Haije, W.G. 149, 152, 157, 228, 248 Spille, H., see Geibel, C. 154, 183 Spiridonov, V.P., see Popenko, N.1. 686 Spirlet, J.C., see Gonçalves, A.P. 148, 169, 268, 269, 272, 286 Spohr, D.A., see Kurti, N. 399 Squires, G.L. 10 Stadelmaier, H.H., see Liu, N.C. 264 Stähler, S., see Attenkofer, K. 114, 115 Staines, M.P., see Tallon, J.L. 475 Staliński, B., see Drulis, M. 181, 183 Stallard, W.A., see Boggis, J.M. 588 Stanley, H.E. 33, 36 Stanton, R.E. 635 Stapleton, H.J., see Fish, G.E. 373 Stapleton, H.J., see Marchand, R.L. 393 Starks, D.F., see Hodgson, K.O. 689 Startsev, S.V., see Anders, A.G. 408 Staub, U., see Allenspach, P. 479 Staub, U., see Guillaume, M. 318, 323, 473 Staub, U., see Mesot, J. 323, 475, 478 Staub, U., see Podlesnyak, A. 318 Staub, U., see Roessli, B. 413 Stauffer, J.L., see Berg, R.A. 665 Stavola, M. 558 Steele, B.C.H., see Bredikhin, S.I. 477

Stefański, P. 209, 232, 233, 243, 244, 247, 250-253 Steglich, F., see Drulis, M. 181, 183 Steglich, F., see Geibel, C. 154, 183 Steglich, F., see Krimmel, A. 150, 152, 154, 162, 181, 183, 184, 189 Steglich, F., see Rauchschwalbe, U. 178, 181-183, 195 Steglich, F., see Suski, W. 185, 268, 272, 282, 283 Steiger, J.J.M. 69 Steiger, J.J.M., see Reimer, P.M. 16 Stein, G., see Haas, Y. 538, 539 Steiner, M., see Dirkmaat, A.J. 459, 469-471 Stelmakhovich, B.M. 146, 154 Stelmakhovich, B.M., see Kuz'ma, Yu.B. 146, 154 Stenger, L., see Morss, L.R. 305 Stenholm, S. 524, 528 Stephen, A.G., see Bleaney, B. 298, 363, 364, 366, 372, 373, 390, 392 Stephens, R.R. 591 St,epień-Damm, J. 148, 152, 169, 177 Sterne, P.A. 473 Sternheimer, R.M. 314 Stetsenko, T.S., see Zvyagin, A.I. 413 Stevens, K.W.H. 308 Stevens, K.W.H., see Mehran, F. 387, 388, 391, 392, 398 Stevens, W.J. 647 Stevens, W.J., see Cundari, T.R. 613, 647, 654, 655, 700, 704 Stevens, W.J., see Krauss, M. 646 Stevenson, M.J., see Sorokin, P.R. 510 Stewart, A.M. 145, 161, 162 Stewart, J.J.P., see Dewar, M.J.S. 651, 699, 704 Sticht, J., see Herman, F. 69 Stohr, J., see Wu, Y. 125 Stokowski, S.E. 575, 579 Stoll, H. 641, 659, 667, 680 Stoll, H., see Bergner, A. 647 Stoll, H., see Dolg, M. 613, 618-620, 625, 628, 629, 640, 647, 648, 651, 653-670, 672-682, 686-688, 692-694, 716 Stoll, H., see Fuentealba, P. 647 Stoll, H., see Igel-Mann, G. 647 Stoll, H., see Kaupp, M. 690, 716 Stoll, H., see Küchle, W. 613, 618, 619, 625, 640, 647,670 Stolov, A.L., see Abdulsabirov, R.Yu. 357, 433 Stolov, A.L., see Bumagina, L.A. 324, 415 Stolov, A.L., see Davidova, M.P. 318, 322-324 Stolov, A.L., see Vinokurov, A.V. 322, 338, 339 Stone, J. 580

Stone, N.J., see Allsop, A.L. 401 Stone, N.J., see Bleaney, B. 401 Stone, N.J., see Clark, R.G. 401 Stone, N.J., see Suzuki, H. 400, 401 Stout, J.W., see Hellwege, K.H. 413 Streczo, G., see Kustov, E.F. 572 Street, R. 126, 140 Street, R., see Muroi, M. 478 Streitwieser, A. 610, 689, 691 Streitwieser, A., see Hodgson, K.O. 689 Streitwieser, A., see Rösch, N. 610, 690 Str, ek, W. 569 Strittmatter, R.J. 690 Strohdecker, L.A., see Cundari, T.R. 718 Struck, C.W. 545 Stryjewski, E. 418 Strzeszewski, J. 263, 265 Strzeszewski, J., see Singleton, E.W. 263, 264 Strzeszewski, J., see Zhao, Z.R. 265 Stucki, F., see Guillaume, M. 318, 323 Sturge, M.D., see Cohen, E. 365 Sucher, J. 636 Sugawa, T., see Komukai, T. 592 Sugawa, T., see Miyajima, Y. 590 Sulkoff, J.W., see Zyskind, J.L. 600 Sumarlin, I.W., see Skanthakumar, S. 413 Sun, H. 258, 259, 265 Sun, H., see Coey, J.M.D. 261 Sun, H., see Yang, Y.-C. 216, 218, 219, 222, 243 Sun, K., see Lee, W.C. 487 Sun, L. 477 Sun, S.H., see Yang, Y.-C. 215, 243, 245 Sun, X.K., see Huang, R.-W. 253 Sunak, H.R.D. 511, 580 Sung Ho Choh, see Bleaney, B. 390, 392 Sungaila, Z., see Dunlap, B.D. 413 Sunopolous, A., see Christides, C. 228, 234 Suscavage, M.J., see Quimby, R.S. 593 Suscavage, M.J., see Yeh, D.C. 593 Suski, W. 148, 150, 154, 155, 157, 168, 169, 178, 181, 183-185, 189, 191, 197, 234, 267, 268, 271-273, 277-283, 286 Suski, W., see Andreev, A.V. 247, 267-270, 274-276, 283-286 Suski, W., see Baran, A. 148, 152-154, 163, 165, 167, 177, 178, 181, 188-190, 194, 195, 267, 268, 271, 273 Suski, W., see Berezyuk, D.A. 147, 233, 234, 237, 240, 242, 243 Suski, W., see Beznosov, A.B. 150, 273 Suski, W., see Bourée-Vigneron, F. 150, 152, 163, 165, 167-169 Suski, W., see Drulis, M. 181, 183 Suski, W., see Geibel, C. 154, 183

Suski, W., see K.epiński, L. 151, 279 Suski, W., see Lunkenheimer, P. 185 Suski, W., see Naydyuk, Yu.G. 151, 181, 183, 189 Suski, W., see Ptasiewicz-B, ak, B. 150, 176, 177, 181-183, 190, 194, 195 Suski, W., see Schäfer, W. 174, 176-178 Suski, W., see St, epień-Damm, J. 148, 152, 169, 177 Suski, W., see Vagizov, F.G. 154, 188, 189, 194, 195, 200-202, 268, 283-285 Suski, W., see Wysłocki, J.J. 246, 247, 267, 268, 271 Suski, W., see Zeleny, M. 162, 200, 267, 268, 273 Suwalski, J., see Baran, A. 267, 268, 271, 273 Suzuki, H. 382, 400, 401, 413 Suzuki, H., see Allsop, A.L. 401 Suzuki, H., see Nakajima, T. 413 Suzuki, M., see Edagawa, E. 587 Suzuki, M., see Tanabe, K. 487, 488 Suzuki, N., see Matsuoka, O. 635 Suzuki, T., see Wu, T.-H. 134-136 Suzuki, Y. 119 Swaddling, P.P., see McMorrow, D.F. 46, 63 Swallow, G.H., see Bleaney, B. 387 Swirles, B. 632, 633 Swithenby, S.J., see Cooke, A.H. 346, 413 Swithenby, S.J., see Gehring, G.A. 458, 459, 466 Syme, R.W.G., see Cockroft, N.J. 559 Sysa, L.V. 146, 206 Szade, J., see Chełkowski, A. 148, 169, 174-176 Szade, J., see Drzazga, Z. 148, 169, 174-176 Szade, J., see Talik, E. 174, 176 Szafranski, C., see Str, ek, W. 569 Szasz, L. 646 Szebesta, D., see Carter, J.N. 590 Szebesta, D., see Lauder, R.D.T. 590 Szebesta, D., see Percival, R.M. 590 Szebesta, D., see Smart, R.G. 592 Szebesta, D., see Whitley, T.J. 592 Szépfalusy, P. 642 Szlaferek, A., see Stefański, P. 253 Szytuła, A. 163 Taga, H., see Wakabayashi, H. 587 Tagirov, L.R., see Eremin, M.V. 325 Tagirov, M.S. 364, 366 Tagirov, M.S., see Abdulsabirov, R.Yu. 364 Tagirov, M.S., see Al'tshuler, S.A. 354, 434, 435 Tagirov, M.S., see Aminov, L.K. 377, 379, 383, 384, 441, 445, 448, 452, 454, 455 Tagirov, M.S., see Antipin, A.A. 382, 384, 385, 390, 392 Tagirov, M.S., see Bakharev, O.N. 479

Tagirov, M.S., see Egorov, A.V. 363, 366-368, 370, 373, 376, 377, 400 Tagirov, M.S., see Korableva, S.L. 362, 364 Tagirov, M.S., see Teplov, M.A. 479 Tagirov, M.S., see Volodin, A.G. 386 Tai, L.T., see Luong, N.H. 215, 252 Tajima, S., see Schutzmann, J. 478 Takahashi, M., see Saito, H. 265 Takahei, K., see Nakagome, H. 597 Takano, Y., see Ishimoto, H. 400 Takayama, S., see Suzuki, Y. 119 Taki, T., see Satoh, M. 317 Talik, E. 174, 176 Talik, E., see Chełkowski, A. 148, 169, 174-176 Talik, E., see Drzazga, Z. 148, 169, 174-176 Tallon, J.L. 475 Tamaki, A., see Goto, T. 351, 354, 357, 358 Tanabe, K. 487, 488 Tanaka, H., see Haruna, M. 599 Tanaka, S., see Schutzmann, J. 478 Tanaka, Y. 25, 30, 31 Tang, N., see Yang, H. 229, 230, 251 Tang, Y.J. 413, 420 Tanimoto, O., see Yokota, M. 554 Tao, W., see Ge, S.-L. 209, 215 Tapster, P.R., see Folinsbee, J.T. 346, 428 Tarasov, E.N., see Andreev, A.V. 148, 156, 215, 221, 222, 245, 246, 248-250, 267, 269 Tarasov, E.N., see Kudrevatykh, N.V. 249 Tassano, J.B., see De Loach, L.D. 549 Tatami, K., see Akayama, M. 215 Tatami, K., see Sun, H. 258 Tatsumi, K., see Pyykkö, P. 684 Tawara, Y., see Kaneko, T. 209, 215 Tawara, Y., see Ohashi, K. 148, 157, 209, 215, 218, 219, 221, 228, 232, 237 Taylor, A., see Guillaume, M. 318, 323 Taylor, A., see Mesot, J. 323 Taylor, A.D., see Podlesnyak, A. 318 Taylor, B.N., see Cohen, E.R. 629 Taylor, D.R. 428, 459 Taylor, D.R., see Folinsbee, J.T. 346, 428 Taylor, D.R., see Graham, J.T. 459 Taylor, D.R., see Harrison, J.P. 346, 428 Taylor, D.R., see Morra, R.M. 428 Taylor, D.R., see Page, J.H. 427, 428 Taylor, D.R., see Reza, K.A. 459, 468 Taylor, P.R., see Dyall, K.G. 635 Tcheou, F., see Abbas, Y. 418 Tcheou, F., see Filippi, J. 413 Tcherbakova, L.G., see Aleksandrov, I.V. 435 Tegus, O., see Li, Q. 209, 210, 218, 247, 249, 269 Tegus, O., see Yang, H. 229, 230, 251

Teichteil, C. 648 Teichteil, C.H. 613 Tejada, J., see Badía, F. 110 Telegina, I.V., see Zolotukhin, O.A. 218 Temmyo, J., see Hattori, K. 599 Teplov, M.A. 298, 363, 364, 370, 479, 487, 489 Teplov, M.A., see Abdulsabirov, R.Yu. 364 Teplov, M.A., see Al'tshuler, S.A. 298, 310, 350, 352-354, 361-365, 377, 382, 386, 389, 434, 435, 444 Teplov, M.A., see Aminov, L.K. 298-300, 363, 368, 372, 377, 379, 381, 383, 384, 390, 392, 393, 396, 397, 441, 445, 448, 452, 454, 455, 483 Teplov, M.A., see Antipin, A.A. 382, 384, 385, 390, 392 Teplov, M.A., see Aukhadeev, F.L. 351, 353, 357, 368, 377, 382, 431, 435, 439 Teplov, M.A., see Bakharev, O.N. 318, 323, 472, 479, 481-483, 486-491 Teplov, M.A., see Dooglav, A.V. 484, 485 Teplov, M.A., see Egorov, A.V. 363, 366-368, 370, 373, 376, 377, 400, 479, 483-485 Teplov, M.A., see Eremin, M.V. 369, 371, 372 Teplov, M.A., see Hirvonen, M.T. 299, 413, 417 Teplov, M.A., see Ishigaki, T. 318, 323 Teplov, M.A., see Konov, I.S. 363, 365, 368, 382 Teplov, M.A., see Korableva, S.L. 362, 364 Teplov, M.A., see Krjukov, E.V. 479, 488, 489 Teplov, M.A., see Kurkin, I.N. 475 Teplov, M.A., see Tagirov, M.S. 364, 366 Teplov, M.A., see Volodin, A.G. 386 Teplov, M.A., see Zhdanov, R.Sh. 367 Terakura, K., see Malozemoff, A.P. 259 Terakura, K., see Williams, A.R. 259 Tereshina, I.S., see Zolotukhin, O.A. 218 Terpilovskii, D.N., see Abdulsabirov, R.Yu. 336, 350 Terpilovskii, D.N., see Al'tshuler, S.A. 310, 350, 352-354, 361, 362, 389, 434, 435 Terpilovskii, D.N., see Aukhadeev, F.L. 351, 353, 357, 435, 439 Teske, C.L., see Haghighi, M.S. 695 Thalmeier, P. 431 Thérianet, S., see Kitagawa, T. 600 Thiel, R.C., see Buschow, K.H.J. 209, 210, 215, 228, 232, 237, 241, 269, 273 Thiel, R.C., see Dirken, M.W. 157, 215, 228, 241, 243 Thiel, W.J., see Dewar, M.J.S. 704 Tholence, J.L., see Caudron, R. 10 Thoma, R.E. 302 Thoma, R.E., see Armbruster, A. 351 Thompson, J.D., see Hundley, M.F. 413 Thompson, J.K., see Kirkwood, A.D. 681

Thomsen, C., see Hadjiev, V.G. 476, 489 Thomsen, C., see Iliev, M. 475 Thomson, T., see O'Grady, K. 126-128 Thony, P., see Sheperd, D.P. 600 Thorn, R.J., see Ackermann, R.J. 651, 666 Thornton, D.D., see Colwell, J.H. 346, 413 Thornton, D.D., see Wright, J.C. 346 Thornton, G. 641 Thorp, T.L., see Cashion, J.D. 346, 408, 413 Thouless, D.J., see Kosterlitz, J.M. 34 Thuy, N.P. 238, 243 Thuy, N.P., see Luong, N.H. 215, 252 Timmer, L.K., see DeKock, R.L. 684, 688, 716 Tippett, L., see Cundari, T.R. 718 Tisza, L., see Luttinger, J.M. 407 Tofield, B.C. 574 Tokunaga, T., see Fujiwara, H. 148, 169, 174, 175 Tolentino, H. 486 Tomey, E. 237, 261 Tomey, E., see Garcia, L.M. 237-239, 246, 247, 2.52 Tomey, E., see Luis, F. 237, 238, 252 Toney, M.F., see Farrow, R.F.C. 21 Tong, F. 591 Tong, F., see Macfarlane, R.M. 591 Torikachvili, M.S., see Rebelsky, L. 272 Toudic, Y., see Auzel, F. 595, 598 Toudic, Y., see Lambert, B. 596 Toudic, Y., see Lhomer, C. 596 Toyozawa, T. 547 Trifonov, E.D., see Malikov, R.F. 529, 533 Triplett, B.B. 414 Triplett, B.B., see Katila, T.E. 413 Triscone, G., see Graf, T. 472, 473, 483, 490 Troć, R., see Fournier, J.-M. 150 Troć, R., see Suski, W. 286 Tromeur, A., see Ronarc'h, D. 588, 589 Tronconi, A.L., see Baker, J.M. 444 Tropper, A.C., see Carter, J.N. 590 Tropper, A.C., see Chartier, I. 600 Tropper, A.C., see Cooke, A.H. 413 Tropper, A.C., see Lauder, R.D.T. 590 Tropper, A.C., see Leask, M.J.M. 413, 429 Tropper, A.C., see Percival, R.M. 590 Tropper, A.C., see Sheperd, D.P. 600 Tropper, A.C., see Smart, R.G. 592 Truhlar, D., see Kahn, L.R. 639, 646 Trusevitch, N.G., see Aleksandrov, I.V. 435 Trygg, J. 157, 160, 161, 257 Tsang, W.T. 597, 598 Tsao, J.Y., see Dodson, B.W. 26 Tschinke, V., see Ziegler, T. 684, 688 Tse, D. 487

Tsui, F. 18, 21, 22, 26-28, 30, 35-37, 65, 66, 68 Tsui, F., see Du, R.-R. 17, 66 Tsui, F., see Everitt, B.A. 10, 14 Tsui, F., see Flynn, C.P. 47, 66 Tsui, F., see Salamon, M.B. 3, 46, 48, 52, 70 Tsujimura, A., see Okamoto, N. 145, 149, 158-160 Tsutai, A., see Sakurada, S. 146, 207, 209 Tsutsumi, K., see Nakajima, T. 413 Tuchendler, J., see Magarino, J. 426, 444 Turek, K., see Baran, A. 267, 268, 271, 273 Tuszyński, M., see Popiel, E.S. 194, 195 Typpi, V.K., see Katila, T.E. 413 Udalov, Yu.P., see Andronenko, S.I. 391 Unoki, H., see Goto, T. 351, 354, 357, 358 Unternahrer, P., see Furrer, A. 318, 323, 422, 475 Unternahrer, P., see Guillaume, M. 318, 323 Upreti, G.C., see Malhotra, V.M. 392 Urland, W. 614, 651 Utton, D.B., see Colwell, J.H. 413 v. Szentpály, L., see Fuentealba, P. 647 Vagin, Y.S. 549 Vagizov, F.G. 154, 188, 189, 194, 195, 200-202, 268, 283--285 Vagizov, F.G., see Andreev, A.V. 269, 274, 275 Vagizov, F.G., see Berezyuk, D.A. 147, 233, 234, 237, 240, 242, 243 Vagizov, F.G., see Suski, W. 157, 234, 268, 273, 279, 280 Vaisfel'd, M.P. 386 Vaishnoras, R.A., see Zvyagin, A.I. 413 Vaknin, D. 479 Valeanu, M., see Burzo, E. 146, 202, 203, 205, 206 Valeanu, M., see Morariu, M. 202, 203, 205 Valeanu, M., see Rogalski, M.S. 202, 205 Valeev, I.I., see Aukhadeev, F.L. 368, 377, 382 Van Bockstal, L., see Janssen, P. 444 van den Hoogenhof, W.N., see Buschow, K.H.J. 148, 152, 153, 165, 167, 174, 177, 181 Van den Hoven, G.N., see Polman, A. 599 van der Kraan, A.M. 148 van der Kraan, A.M., see Buschow, K.H.J. 148. 169, 174–178 van der Kraan, A.M., see Gubbens, P.C.M. 209, 215, 228, 232, 233, 253, 257, 275 Van der Merwe, J.H. 26 Van der Ziel, J.P. 557, 597 van Dover, R.B. 94 van Dover, R.B., see Hellman, F. 119 van Eijk, C.W.E., see Andriessen, J. 714, 716 van Engelen, P.P.J. 150, 270

Van Landuyt, J., see Reyes-Gasga, J. 474, 475, 478 van Leeuwen, R., see Van Lenthe, E. 638 Van Lenthe, E. 638 Van Piggelen, H.U. 707 van Schilfgaarde, M., see Herman, F. 69 Van Tendeloo, G., see Krekels, T. 478 Van Tendeloo, G., see Reyes-Gasga, J. 474, 475, 478 Van Uitert, L.G., see Birgeneau, R.J. 365 Van Uitert, L.G., see Cohen, E. 365 Van Uitert, L.G., see Lyons, K.B. 365 Van Uitert, L.G., see Riseberg, L.A. 365 Van Uitert, L.G., see Singh, S. 538 Van Uitert, L.G., see Van der Ziel, J.P. 557 Van Vleck, J.H. 347 van Vucht, J.H.N., see Buschow, K.H.J. 148, 152, 153, 165, 167, 174, 177, 181 van Wazer, J.R., see Datta, S.N. 643 van Wezenbeek, E.M., see Schwarz, W.H.E. 615, 617 van Wingerden, D.J., see Pinkerton, F.E. 264 Van Zee, R.J. 658, 666, 667, 679, 680 Vanderven, N.S., see Petasis, D.T. 346, 413, 428 Varsanyi, F. 544 Vasil'ev, A.V. 459, 466, 467 Vasil'ev, A.V., see Sokolov, V.I. 459, 466-468 Vazquez, J.E., see Beyers, R. 474, 475 Veal, B.W. 475, 478, 488 Veal, B.W., see Jorgensen, J.D. 471, 475, 476, 478, 488 Veal, B.W., see Mogilevsky, R. 489 Veal, B.W., see Yang, S. 478 Vedrine, A. 305 Veenendaal, E.J. 305, 366, 367, 413 Veillard, A. 612 Vekhter, B.G. 360, 361, 429 Vekhter, B.G., see Bondar', I.A. 355, 356, 359, 360 Vekhter, B.G., see Ioffe, V.A. 360 Vekhter, B.G., see Kaplan, M.D. 360 Verdini, L., see Cannelli, G. 477 Verhoef, R. 135, 149, 156, 215, 228, 232, 233, 237, 241, 246, 257 Vernooijs, P., see DeKock, R.L. 684, 688, 716 Verweij, M., see Reyes-Gasga, J. 474, 475, 478 Vettier, C. 46 Vettier, C., see Abbas, Y. 413, 418 Vettier, C., see Gibbs, D. 6, 10, 13, 16 Vettier, C., see Kwo, J. 3, 14, 20, 39, 47 Vettier, C., see Majkrzak, C.F. 39, 44, 46-48, 60 Veuro, M.C., see Katila, T.E. 413 Vial, J.C. 559 Viana, R., see Lunkenheimer, P. 185

Victora, R.H., see Falicov, L.M. 20, 32, 35, 47 Vijayaraghavan, R., see Malik, S.K. 174, 175 Vinokurov, A.V. 322, 338, 339 Vinokurov, A.V., see Abdulsabirov, R.Yu. 357, 433 Vinokurov, A.V., see Aminov, L.K. 300, 390, 392, 393, 396, 397 Vishwamittar, X. 302 Visscher, L. 613, 635, 708 Visscher, L., see DeJong, W.A. 635, 707 Visscher, L., see Nieuwpoort, W.C. 635, 636 Visscher, L., see Visser, O. 613, 614, 632, 706-710, 712, 716 Visser, O. 613, 614, 631, 632, 706-710, 712, 716 Visser, O., see DeJong, W.A. 635, 707 Visser, O., see Visscher, L. 635 Visser, R. 710, 712, 713, 716 Viswanathan, C.R. 392 Vleggan, J.J.M., see Helmholdt, R.B. 149, 156, 228, 255 Vodjani, N., see Charasse, M.N. 594 Vogtlin, K., see Hess, G. 459, 466, 467 Volodin, A.G. 386 Volodin, A.G., see Al'tshuler, S.A. 354, 434, 435 Volodin, A.G., see Aminov, L.K. 441, 445, 448, 452, 454, 455 Volodin, A.G., see Bakharev, O.N. 318, 323, 472, 479, 481-483, 486-491 Volodin, A.G., see Teplov, M.A. 479, 487, 489 Volotskii, S.V., see Anders, A.G. 408, 421 Von Arnim, M. 643 Voronkova, V.I. 475 Vosko, S.H. 641, 659, 667, 680, 715 Vosko, S.H., see Wijesundera, W.P. 623 Vredenberg, A.M., see Schubert, E.F. 600 Vrehen, Q.H.F., see Polder, D. 526, 531 Vu Hoang Chau, see Chapellier, M. 401 Waber, J.T. 623 Waber, J.T., see Mann, J.B. 612 Wachter, P. 490 Wada, H. 168 Wada, M., see Hattori, K. 599 Wadt, W.R. 639, 646, 684 Wadt, W.R., see Hay, P.J. 639, 646, 661, 665, 684, 688, 699, 700 Waerenborgh, J.C., see Gonçalves, A.P. 268, 269, 272, 286 Wagener, D., see Bakharev, O.N. 318, 323, 472, 479, 481-483, 486-491 Wagener, D., see Dooglav, A.V. 484, 485 Wagener, D., see Egorov, A.V. 479, 483-485 Wagener, D., see Krekels, T. 478 Wagener, D., see Teplov, M.A. 479, 487, 489

Wagner, J., see Ennen, H. 594, 595 Wagner, M., see Mutscheller, W. 329 Wahlgren, U., see Marian, C.M. 670 Waite, T. 512 Wakabayashi, H. 587 Wakabayashi, H., see Edagawa, E. 587 Wakiyama, T., see Saito, H. 265 Walker, P.J., see Beauvillain, P. 346, 425 Walker, P.J., see Bleaney, B. 298, 363, 364, 366, 372, 373, 390 Walker, P.J., see Suzuki, H. 401 Wallace, W.E. 261 Wallace, W.E., see Cheng, S.F. 218 Wallace, W.E., see Sinha, V.K. 215, 216, 218, 219, 221, 222, 248 Wallace, W.E., see Zhang, L.Y. 248, 249 Waller, I. 380 Wallmeier, H. 638 Wallmeier, H., see Schwarz, W.H.E. 633, 635 Walsh, A.D. 684, 688 Walsh, P.N., see Ames, L.L. 660 Wan, Z., see Lin, C. 209, 271, 272, 278 Wang, F., see Li, Z. 610, 705 Wang, F.C. 145 Wang, Jing-tang 265 Wang, L., see Chai, Y. 696, 699 Wang, S., see Li, Z. 610, 705 Wang, S.G. 613, 620, 625, 626, 629, 641, 659, 660, 665, 667, 672, 675, 680, 716 Wang, T., see Hu, J. 149, 155, 156, 215, 216, 220, 237, 248, 251 Wang, X., see Li, L. 610, 613, 649, 685, 706 Wang, X., see Ren, J. 613, 649 Wang, Xian-zhong 194, 197 Wang, Y. 599 Wang, Y., see Sun, L. 477 Wang, Y.J. 82, 125, 136-138 Wang, Y.J., see Shan, Z.S. 98, 99, 105, 116-118, 121, 122, 124 Wang, Y.J., see Zhang, H.Y. 91 Wang, Y.Y., see Zhang, H. 475 Wang, Y.Z. 228, 263, 264 Wang, Y.Z., see Hu, J. 149, 155, 156, 215, 216, 220, 251 Wang, Y.Z., see Strzeszewski, J. 263, 265 Wang, Z., see Hu, J. 218, 237, 248 Wang, Z.X., see Hu, J. 149, 155, 156, 215, 216, 220, 251 Wang Xue-feng, see Yan Yu 244 Wangsness, R.K. 379 Wanklyn, B.M. 408, 413 Wanklyn, B.M., see Sen, H. 319 Wannemacher, R. 531 Wannemacher, R., see Hebert, T. 564, 591

Warbuton, T.J., see Sheperd, D.P. 600 Ward, R.C.C., see Bleaney, B. 408 Ward, R.C.C., see Brown, P.J. 413, 416 Ward, R.C.C., see Jehan, D.A. 25, 54 Ward, R.C.C., see Leask, M.J.M. 415, 416 Ward, R.C.C., see McMorrow, D.F. 46, 63 Ward, R.C.C., see Simpson, J.A. 46, 65 Warren, K.D. 690 Warren, K.D., see Clack, D.W. 610, 649, 690 Wassermann, E.F., see Scholz, B. 109, 111, 112 Wästberg, B., see Rosén, A. 697, 698, 716 Waszczak, J.V., see Kwo, J. 21, 22, 30, 47 Waszczak, J.V., see Majkrzak, C.F. 39, 44, 46-48, 60 Watson, P.L., see Jahns, V. 649, 703, 717 Watson, R.E., see Blume, M. 639 Watson, R.E., see Freeman, A.J. 322, 324 Watson, R.E., see Melamud, M. 151, 157 Watts, B.E., see Taylor, D.R. 459 Weaver, J.H., see Guo, T. 696 Weaver, J.M.R., see Bleaney, B. 387 Weber, G., see Bonrath, H. 413 Weber, H.P., see Danielmeyer, H.G. 567 Weber, H.P., see Tofield, B.C. 574 Weber, J. 610, 706 Weber, M.J. 510, 540, 544, 554 Weber, M.J., see Stokowski, S.E. 575, 579 Weber, R.T., see Baker, J.M. 444 Weber, T., see Metzger, J. 477 Wechsel-Trakowski, E., see Hafner, P. 622 Wechsel-Trakowski, E., see Schwarz, W.H.E. 635 Wecker, J., see Katter, M. 265 Wecker, J., see Schnitzke, K. 266 Wecker, J., see Schultz, L. 264-266 Wedgwood, F.A., see Elliott, R.J. 6 Wedig, U., see Dolg, M. 647 Weeks, J.D. 646 Wehcle, H., see Armbruster, A. 351 Wei, J., see Guan, W.Y. 413 Weidinger, A., see Reimer, P.M. 16 Weiss, A., see Schmidt, P.G. 317, 324 Weissbluth, M. 516, 519, 521 Weissbuch, C., see Charasse, M.N. 594 Weitzer, F. 146, 202, 203, 205, 206 Welipitiya, D., see Fernando, A.S. 215, 228, 232, 258 Weller, D., see Wu, Y. 125 Weller, J., see Kaufman, U. 595 Weller, P.F., see Axe, J.D. 552 Wells, M.R., see Abraham, M.M. 445 Wells, M.R., see Baker, J.M. 391, 444 Wells, M.R., see Bleaney, B. 298, 318, 322, 351, 363, 364, 366–368, 372, 373, 387, 390, 392, 408, 413, 416, 429

Wells, M.R., see Brown, P.J. 413, 416 Wells, M.R., see Cashion, J.D. 346, 408, 413 Wells, M.R., see Cooke, A.H. 346, 413, 420 Wells, M.R., see Gehring, G.A. 458, 459, 466 Wells, M.R., see Jehan, D.A. 25, 54 Wells, M.R., see Leask, M.J.M. 413, 415, 416, 429 Wells, M.R., see McMorrow, D.F. 46, 63 Wells, M.R., see Simpson, J.A. 46, 65 Welp, U. 475 Welp, U., see Rothman, S.J. 475 Weltner, W., see DeKock, L. 666 Weltner, W., see Van Zee, R.J. 658, 666, 667, 679, 680 Weng, C.C., see Chin, T.S. 209, 215, 228, 232, 237 Wernick, J.H., see McHenry, M.R. 487 Wesley, R.D., see DeKock, C.W. 686, 687 Wharton, L., see Berg, R.A. 665 Wheatley, J.C. 399 Wheeler, R., see Yang, S. 478 White, D., see Ames, L.L. 660 White, R., see Lottis, D.K. 130 White, R.M., see Triplett, B.B. 414 White, S.J., see Corruccini, L.R. 408, 413, 421 White, S.J., see Roser, M.R. 413, 417 Whitehead, J.P., see De'Bell, K. 422 Whitehead, J.P., see MacIsaac, A.B. 421 Whitley, T.J. 592 Wickramasekara, L., see Kamprath, N. 264, 266 Wickramasekara, L., see Liu, N.C. 264 Wielinga, R.F., see Blöte, H.W.J. 413 Wiesinger, G., see Attenkofer, K. 114, 115 Wiesler, D.G., see Farrow, R.F.C. 21 Wijesundera, W.P. 623 Wilk, L., see Vosko, S.H. 641, 659, 667, 680, 715 Wilkinson, G., see Cotton, F.A. 690 Will, G. 304, 413, 419 Will, G., see Gal, J. 150, 154, 163, 165, 174, 176-178, 181, 182, 185, 201 Will, G., see Halevy, I. 186-189, 202 Will, G., see Kockelmann, W. 154, 185-188, 413 Will, G., see Schäfer, W. 174, 176-178, 185 Wille, L.T., see Fontaine, D. 473 Wille, L.T., see Sterne, P.A. 473 Williams, A.R. 259 Williams, A.R., see Malozemoff, A.P. 149, 259 Williams, H.J., see MacChesney, J.B. 413 Williams, J.M., see Broach, R.W. 302, 303, 370, 448 Williams, J.R., see Percival, R.M. 590 Wilson, S. 612, 635 Wiltshire, M.C.K., see Bleaney, B. 363, 366 Windsor, C.G., see Hutchings, M.T. 392

Winiarska, A., see Chełkowska, G. 194, 195 Winiarska, A., see Chełkowski, A. 148, 169, 174 - 176Winiarska, A., see Jelonek, J. 194, 195 Winiarski, A., see Chełkowski, A. 148, 169, 174-176 Winter, N.W., see Pitzer, R.M. 645, 648 Wise, P.P., see Bulman, J.B. 413 Wisniewski, M.-U., see Sinnemann, Th. 209, 228 Witters, J., see de Groot, P. 444 Witteveen, J., see Bakharev, O.N. 479, 488, 489 Witteveen, J., see Teplov, M.A. 487, 489 Włosewicz, D., see Suski, W. 272, 279, 280, 282, 283 Wochner, P., see Tanaka, Y. 25, 30, 31 Wochowski, K., see Berezyuk, D.A. 147, 233, 234, 237, 240, 242, 243 Wochowski, K., see K, epiński, L. 151, 279 Wochowski, K., see Suski, W. 150, 154, 157, 168, 181, 183-185, 189, 191, 197, 234, 268, 271-273, 277-283 Wochowski, K., see Vagizov, F.G. 154, 188, 189, 194, 195, 200-202 Wochowski, K., see Wysłocki, J.J. 247 Wohlleben, D., see Braunisch, W. 478 Wolf, P., see Cordier, G. 181 Wolf, S.A., see Osofsky, M.S. 478 Wolf, T., see Metzger, J. 477 Wolf, T., see Schreiner, Th. 489 Wolf, T., see Zeiske, T. 475 Wolf, W.P. 413, 429 Wolf, W.P., see Catanese, C.A. 343, 346, 413 Wolf, W.P., see Cochrane, R.W. 392 Wolf, W.P., see Cone, R.L. 343 Wolf, W.P., see Cooke, A.H. 404, 405, 413, 417 Wolf, W.P., see Fillion, G. 413, 428 Wolf, W.P., see Folinsbee, J.T. 346, 428 Wolf, W.P., see Hutchings, M.T. 343, 387, 390, 392 Wolf, W.P., see Skjeltorp, A.T. 346, 413 Wolfe, J.P. 453, 457 Wolfe, J.P., see King, A.R. 456 Wolfsberg, M. 317, 685 Wollan, E.O., see Cable, J.W. 14 Wong, E.Y., see Viswanathan, C.R. 392 Wong, Y.H., see Schubert, E.F. 600 Wood, D.L., see Kaiser, W. 510 Wood, J.H. 617, 639 Wood, J.H., see Boring, A.M. 640, 690, 715 Woodcock, R., see Snitzer, E. 510, 556 Woodfield, B.F., see Phillips, N.E. 490, 491 Woods, J.P., see Fernando, A.S. 215, 228, 232, 258 Woolley, J.C., see Street, R. 126, 140

Wordland, W.A., see Riseberg, L.A. 365 Wörmer, R., see Kaufman, U. 595 Wortmann, G. 413 Wouthuysen, S.A., see Foldy, L.L. 636 Wright, D.A., see Emerson, J.P. 490 Wright, D.A., see Phillips, N.E. 490, 491 Wright, J.C. 346 Wrzeciono, A., see Stefański, P. 232, 233, 243, 244, 253 Wu, C.D., see Huang, S.H. 263 Wu, C.Y., see Cochrane, R.W. 392 Wu, M.K., see Guan, W.Y. 413 Wu, N., see Dong, N. 705, 717 Wu, T.-H. 134-136 Wu, W. 458, 469 Wu, W., see Rosenbaum, T.F. 458 Wu, X., see Zeng, Y. 218 Wu, Y. 125 Wu, Z.L., see Xie, X.M. 475 Wuchner, W., see Bohm, W. 322 Wuchner, W., see Gehring, G.A. 346, 413, 417, 419 Wuchner, W., see Laugsch, J. 343, 346 Wühl, H., see Claus, H. 478 Wuhl, H., see Metzger, J. 477 Wun, M., see Hirvonen, M.T. 299, 413, 417 Wyart, J.-F., see Blaise, J. 612 Wyatt, A.F.G., see Wolf, W.P. 413 Wyatt, R., see Whitley, T.J. 592 Wyatt, R.S., see Beattie, I.R. 686, 687 Wybourne, B.G. 125 Wysłocki, J.J. 246, 247, 267, 268, 271 Xia, J.-B. 70 Xie, X.M. 475 Xu, G. 610, 649, 703, 705 Xu, G., see Huang, L. 705 Xu, G., see Li, J. 610, 695 Xu, G., see Li, L. 610, 613, 649, 685, 706 Xu, G., see Li, Z. 610, 705 Xu, G., see Ren, J. 610, 613, 649, 705 Xu, H.-J. 418 Xu, J. 413, 417 Xu, J., see Roser, M.R. 413, 417 Xu, Xie 237, 238 Xu, Y., see Cheng, S.F. 218 Xu, Z.X., see Geng, M.M. 237 Xu, Z.X., see Ma, R.H. 209, 228, 247 Xue, R.H., see Solzi, M. 207, 209, 210, 218, 221, 247 Yaar, I., see Gal, J. 150, 154, 174, 176-178, 185, 201 Yaar, I., see Halevy, I. 186-189, 202

Yadaralli, S., see Flynn, C.P. 47 Yadav, B.R. 666 Yadavalli, S., see Flynn, C.P. 16 Yafet, Y. 7, 48, 50, 69, 71 Yafet, Y., see Kwo, J. 21, 22, 30 Yafet, Y., see Majkrzak, C.F. 3, 39, 44, 46-48, 54, 60, 65 Yagfarov, M.Sh., see Zhdanov, R.Sh. 367 Yagudin, Sh.1., see Zhdanov, R.Sh. 367 Yamabe, S., see Hosoya, H. 611 Yamada, M., see Kaneko, T. 209, 215 Yamada, N. 553 Yamagishi, K., see Okada, M. 209, 228, 232, 233, 237 Yamamoto, K., see Akayama, M. 215 Yamamoto, S., see Wakabayashi, H. 587 Yamamoto, T., see Komukai, T. 592 Yamamoto, Y. 527 Yamauchi, K. 90 Yan, X. 119 Yan, X., see Zeng, Y. 218 Yan Yu 244 Yang, C.Y. 641, 706 Yang, F.-M. 232, 233, 248, 249 Yang, F.M., see Li, Q. 209, 210, 218, 247, 249, 269 Yang, F.M., see Yang, H. 229, 230, 251 Yang, G.Q., see Ge, S.-L. 209, 215 Yang, H. 229, 230, 251 Yang, J., see Reich, D.H. 458, 469-471 Yang, J., see Rosenbaum, T.F. 458 Yang, J.-L., see Lin, C. 209, 271, 272, 278 Yang, J.-L., see Yang, Y.-C. 216, 261 Yang, K.N. 413 Yang, M.-H. 3, 15 Yang, S. 478 Yang, X., see Hu, J. 237, 248 Yang, Y., see Ge, S.-L. 209, 215 Yang, Y., see Yang, Y.-C. 237 Yang, Y.-C. 215, 216, 218, 219, 222, 237, 243, 245, 261, 263 Yang, Y.-C., see Ge, S.-L. 209, 215 Yang, Y.C. 148, 233 Yang, Y.C., see Li, Z.W. 219, 222 Yannoni, C.S., see Johnson, R.D. 699 Yannoni, C.S., see Macfarlane, R.M. 531 Yanovskii, V.K., see Voronkova, V.I. 475 Yanson, I.K., see Naydyuk, Yu.G. 151, 181, 183, 189 Yariv, A. 526, 580 Ye, C.-T., see Yang, Y.-C. 216, 261 Yeh, D.C. 593 Yellon, B.W. 258 Yelon, W., see Yang, Y.C. 233

Yen, W.M. 549 Yermolenko, A.S., see Scherbakova, Ye.V. 237, 238, 248 Yoden, K. 90, 112, 113 Yokota, M. 554 Yokoyama, T., see Ohashi, K. 148, 215 Yokozeki, A. 673, 674, 679 Yoneda, Y., see Ohashi, K. 216, 233 Yoo, S.I., see Allenspach, P. 413, 422 Yoshida, H., see Kaneko, T. 209, 215 Yoshida, N., see Streitwieser, A. 689 Yoshie, H., see Amako, Y. 158, 159 Yoshie, H., see Okamoto, N. 145, 149, 158-160 Yoshimura, K., see Wada, H. 168 Yoshioka, Y., see Ohta, K. 643 Yoshiyama, M., see Honda, S. 90 You, H., see Veal, B.W. 475, 478, 488 Young, A.P. 329 Youngblood, R.W. 468 Yu, M.-J., see Yang, H. 229, 230, 251 Yurko, V.G., see Zvyagin, A.I. 413 Yvon, K., see Gueramian, M. 154, 156, 242, 243, 246, 268, 273

Zabel, H., see Flynn, C.P. 47 Zabel, H., see Reimer, P.M. 16 Zabenko, V.V., see Zolotukhin, O.A. 218 Zaleski, A., see Suski, W. 185, 268, 272, 282, 283 Zalewski, A., see Suski, W. 154, 168, 183, 189, 191, 197 Zalubas, R., see Martin, W.C. 609, 612, 619, 652-654, 671, 682, 701 Zarechnyuk, O.S. 146-148, 157 Zarek, W., see Jelonek, J. 194, 195 Zarek, W., see Popiel, E.S. 194, 195 Zarestky, J.L., see Vaknin, D. 479 Zasorin, E.Z., see Krasnov, K.S. 686 Zasorin, E.Z., see Popenko, N.I. 686 Zayhowski, J.J. 567, 599 Zdanovitch, S.B., see Davidova, M.P. 318, 323 Zeiske, T. 475 Zeleny, M. 162, 200, 267, 268, 273 Zeng, Y. 218 Zeper, W.B., see Schütz, G. 140 Zeringue, K.J., see Van Zee, R.J. 666, 667 Zerner, M.C., see Cory, M.G. 614, 649 Zerner, M.C., see Culberson, J.C. 610, 613, 649, 685, 686, 688, 703 Zerner, M.C., see Kotzian, M. 613, 648, 649, 663, 665, 666, 668, 669, 701, 702, 717 Zerner, M.C., see Salahub, D.R. 612 Zhang, B.S., see Lin, C. 209, 271, 272, 278

Zhang, B.S., see Yang, Y.-C. 216, 261 Zhang, H. 413, 421, 475 Zhang, H., see Skanthakumar, S. 413 Zhang, H.Y. 91 Zhang, J., see Li, D.Q. 35 Zhang, K., see Dunlap, B.D. 413 Zhang, K., see Mogilevsky, R. 489 Zhang, K., see Zhang, H. 475 Zhang, L.Y. 248, 249 Zhang, M.W., see Yang, Y.-C. 237 Zhang, O.L. 696 Zhang, S.G., see Hu, J. 149, 155, 156, 215, 216, 220, 251 Zhang, S.G., see Jia, Y.Q. 651 Zhang, X.-D., see Yang, Y.-C. 237, 261, 263 Zhang, X.X., see Badía, F. 110 Zhang, Z.-D., see Huang, R.-W. 253 Zhang, Z.-J., see Yang, Y.-C. 218, 219, 222, 243 Zhang, Z.-W., see Huang, R.-W. 253 Zhang, Z.D., see Verhoef, R. 149, 156, 215, 228, 232, 233, 237, 241, 246, 257 Zhao, F., see Scott, B.P. 591 Zhao, H., see Hu, J. 237, 248 Zhao, K., see Chang, A.H.H. 648, 691, 697 Zhao, R.-W., see Yang, F.-M. 232, 233, 248, 249 Zhao, R.W., see Li, Q. 209, 210, 218, 247, 249, 269 Zhao, Z.G. 135 Zhao, Z.R. 265 Zhdanov, R.Sh. 367 Zhdanov, R.Sh., see Al'tshuler, S.A. 354, 434, 435 Zhdanov, R.Sh., see Aukhadeev, F.L. 351, 353, 357, 431, 435, 439

Zhdanov, R.Sh., see Kurkin, I.N. 475 Zhdanov, R.Sh., see Teplov, M.A. 479 Zheng, G.G., see Zhang, H.Y. 91 Zhokhov, A.A., see Bredikhin, S.1. 477 Zhong, J.S., see Ge, S.-L. 209, 215 Zhorin, V.V., see Avanesov, A.G. 323, 324 Zhou, B.W. 598 Zhou, G. 18 Zhou, G.F., see Brabers, J.H.V.J. 228, 229 Zhou, P., see Egami, T. 94 Zhou, X.Z., see Li, Z.W. 218, 219, 222 Zhu, J.G., see Bertram, H.N. 132 Zhu, L., see Dong, N. 705, 717 Zhu, X., see Flynn, C.P. 47 Ziegler, T. 619, 684, 688 Zoebisch, E.G., see Dewar, M.J.S. 651, 699, 704 Zogał, O.J., see Baran, A. 181 Żogał, O.J., see Suski, W. 150, 268, 272, 279 Zolin, V.F., see Markushev, V.M. 538 Zolliker, M., see Roessli, B. 413 Zolotukhin, O.A. 218 Zou, H., see Krekels, T. 478 Zouganelis, G., see Christides, C. 228, 234 Zounova, F., see Zeleny, M. 162, 200, 267, 268, 273 Zuber, J.-B., see Itzykson, C. 629 Zvyagin, A.I. 413 Zvyagin, A.I., see Pshisukha, A.M. 413 Zwartz, E., see Taylor, D.R. 459 Zvdzik, G.J., see Schubert, E.F. 600 Zygmunt, A., see Suski, W. 150, 268, 272, 279 Zyskind, J.L. 600 Zyskind, J.L., see Desurvire, E. 587 Zyskind, J.L., see Giles, C.R. 587

776

SUBJECT INDEX

APTE effect (Addition de Photon par Transferts d'Energie) 558, 559, 579, 585, 590, 591, 593, 596 ASE (amplified spontaneous emission) 512, 532, 536-540 see also powder ASE - doped fibres 537 - LiNdPO₃ 539 - (MoO₄)₄Na₅Nd 538 - NdCl3:6H2O 538 - Nd_{0.75}La_{0.25}P₅O₁₄ 539 - NdP5O14 539 - R-doped media 537 - R-doped powders 538 - Schuurmans-Polder condition 537 actinide - contraction 622-627 - ground state 612 - ThMn₁₂ compounds 267 admixture of the lanthanide atom in other positions 157 agostic interaction 704 all-electron methods 630 α -Fe–Co(–Si) alloy, Sm₂Fe_{17 – r}Co_r 210 aluminates, RAIO₃ 418 aluminides 154, 162-202 amorphous magnetism 265 amorphous materials 265 - ribbons 263 - thin film 185 amplification - 3-level 580 - at 1.5 µm 587 amplifier wave lengths observed in silica and fluoride fibers 593 AnFe₄Al_{8-x} 176 AnFe₄Al₈ 150 AnFe_{4+x}Al_{8-x} compounds 154 AnFe₄Al₈ series 150 angular overlap model 614, 650 anisotropy 207, 219, 243-246, 252, 277, 286 - axial 212-214, 216-218, 225, 227, 236, 242, 252 - basal-plane 248, 284 - constants 219, 244, 246, 249, 250, 270

- demagnetization anisotropy in multilayers 133 - energy 244, 249 - exchange 343 - field 206, 231, 244-246 - interface anisotropy, see interface anisotropy - layer-thickness dependence - - for Dy/Co multilayers 97-99 - - for Dy/Fe multilayers 94 - - for Tb/Fe multilayers 101 - magnetocrystalline, total 284 - measurements of anisotropy near the compensation point 94, 134, 135 - perpendicular anisotropy, see perpendicular magnetic anisotropy (PMA) - planar 216, 217, 236, 242, 266 – sign of 247 - temperature dependence for Tb/Fe multilayers 104 - total 249 - type 249, 284 -- change 283 - uniaxial 245, 265 - - energy 267 - - magnetocrystalline 271 anti-Stokes lasers 591 - in fluoride glass fibers 591 anti-Stokes process 590 antiferromagnetic resonance in dielectric compounds 401, 445 arsenates, RAsO₄ 304, 325, 339, 419 atom-field interaction 512 atomic calculations 651-655 Auger effect 596 augmented-spherical-wave method 256 average magnetic valence 259 axial anisotropy 212-214, 216-218, 225, 227, 236, 242, 252 Ba2MgGe2O7 573 BaY₂F₈ 591 band-structure calculations of ThMn12-type

see also DOS, LMTO, LSD, self-consistent spin-polarization calculations, semirelativistic approximation, tight-binding calculations

compounds 252-261

compounds (cont'd) - band magnetism 257 - band structure 252, 286 - bandwidth 261 - effect on the physical properties 283 - nonrelativistic approximation 258 - self-consistent 256, 257 basal-plane anisotropy 248, 284 (Bd, La)Ta7O19 573 binary compounds with Fe, lattice parameters, magnetic properties 160, 161 binary compounds with Mn, magnetic properties 158-160 binary compounds with Zn, lattice parameters, magnetic properties 160-162 bis(η^5 -cyclopentadienyl)ytterbium(III) 703 bis(η^5 -methylcyclopentadienyl)ytterbium chloride 695 bis(η^5 -pentamethylcyclopentadienyl)samarium 695 Bloch longitudinal relaxation time (T_1) 523, 524 Bloch transverse relaxation time (T_2) 523, 524, 531, 535, 600 bond length - contraction 619 - expansion 619 bond strength 572 Born-Oppenheimer approximation 545 boron addition 263 branching ratios 543, 576, 577 Breit-Pauli Hamiltonian 637 Breit term 631 broad existence range - aluminides 154 - cobalt ternary compounds 156 - gallides 154 - iron ternary compounds 154, 156 - manganese ternary compounds 156 - nickel ternary compounds 156 bromates, R(BO₃)₃·9H₂O 343, 409, 418 Brown-Ravenhall disease 636 CEF (crystalline electric field) 5, 7, 10, 14, 190, 243, 246, 252, 307, 571 - analysis 212 angular overlap model 313 - calculations 255 - changes near impurity ions 300, 398 - consideration 276 - effects 182, 190, 244, 272, 283 - exchange charge model 314, 317, 322, 324, 427 - interactions 243

band-structure calculations of ThMn₁₂-type

- invariants 571 - levels in ErNi₁₀Si₂ 209 – model 277 -- point-charge 255 - of point multipoles 314, 317 - parameters 244, 246, 249, 253, 308, 312, 322, 325, 572 - - for DyBa₂Cu₃O₇ 323 - for Dy_{1-x}Gd_xFe₁₁Ti 251 - - for ErBa₂Cu₃O₆ 323 - - for ErBa₂Cu₃O₇ 323 -- for GdFe_{12-x}W_x 241 -- for HoBa₂Cu₃O₇ 323 - - for HoPO₄ 322 - - for HoVO₄ 322 - - for LiDyF₄ 323 - - for LiErF₄ 323 - - for LiHoF₄ 323 - - for LiTbF₄ 323 – – for LiTmF₄ 323 -- for R(Fe, Co)_{12-x}Mo_x 235 -- for R(Fe, Co)_{12-x}V_x 224–226 - - for RFe₁₀Cr₂ 232 -- for RFe_{12-r}Ti_r 211–214 -- for $RM_{10}Si_2$ 208, 209 -- for TbAsO₄ 322 - - for TbPO₄ 322 - - for TbVO₄ 322 - - for TmAsO₄ 322 $- - \text{for TmBa}_2\text{Cu}_3\text{O}_{6+x}$ 323, 479 - - for TmBa₂Cu₄O₈ 479 - - for Tm³⁺ in TmVO₄:Tb³⁺ 463 - - for TmPO₄ 322 - - for TmVO₄ 322 -- for YbBa₂Cu₃O₇ 323 - potentials 243, 244 - quadrupole component 313, 315, 324, 399 - random 457, 459, 461, 483 - - distribution function 459, 462, 467 - shielding factors 314 - strength 567 - superposition model 313 - terms 250, 252 - weak 182 CLAP 573 CW laser UV sources 599 CaAl₄O₇ 573 CaF₂ 573 CaF2-CdF3 576 Ca₅(PO₄)₃F (FAP) 573 carbides, $Sm_xFe_vC_z$ 266 carbon substitution in RFe11 Ti 261-263 cascaded fluoride amplifier 590 Ce^{3+} , in CaF_2 712

 Ce^{4+} , electronic states 710 Ce"+, in CaF₂, BaF₂ 713 Ce, valence spinors 623 Ce-Co-Mn 156, 157 Ce--Cr--Al 154 Ce-Fe-Mn 156 Ce--Fe--Mo 157 Ce-Fe-Re 156 Ce-Mn-Ni 156 CeAg₄Al₈ 195 CeBr₃ 344 $Ce(C_8H_8)_2$, see cerocene CeCl₃ 344 CeCl₃:Nd³⁺ 538 CeCo10Mo2 236 CeCo₁₁Ti 216 CeCr₄Al₈ 164 CeCu₄Al₈ 178-180, 182 CeF 677 CeF₃ 706 CeF⁺₂ 706 CeF₈⁵⁻ 706 $CeF_{0}^{(8-n)-}$ 711 CeFe₄Al₈ 170 Ce2Fe14B 234 CeFe_xGa_{12-x} 204 CeFe5.4Ga6.6 206 CeFe₁₀Mo₂ 233, 234 CeFe_{12-r}Mo_r 235 Ce1.33 Fe8.8 Mo3.2 233, 234 $Ce_{1-x}Fe_x$ phase 234 $CeFe_{12-r}Re_2$ 242 Ce1.33Fe10Re2 242 $CeFe_{12-x}Ti_x = 211$ $CeFe_{11}TiC_{1-x}$ 262 $CeFe_{12-x}V_x$ 223 CeH₄ 684 $[Ce(H_2O)_n]^{3+}$ 700 - electronic states for n=9 702 CeMn₄Al₈ 166 $Ce(NO_3)_6^{2}$ 703 CeO 668 - electronic states 664, 668, 669 - orbital analysis 663 - population analysis 670 - spectroscopic constants 664, 668 CeO₂ 684 CeO_{2}^{+} 684 Ce@C28 696 cerium-di-phthalocyanine, structure 695 cerocene ($Ce(C_8H_8)_2$) 689, 690 – anion 690 electronic states 693, 694

- geometry 693 - structure 691 chlorides, hydrated 409 Cl₂LaH 704 Cl₂LuH 704 Cl₃Nd in ice 573 Cl₂RH 704 Cl₂ScH 704 Cl₂YH 704 clusters 531 Co10V2 229 coercivity in ThMn₁₂-type compounds 264-266 - random-anisotropy model 265 coherence length - magnetic 42, 51, 52, 70 - structural 51 coherent emission 507-600 coherent photon-echo techniques 553 coherent pumping 525 compensation point see also magnetization - Dy/Co multilayers 96, 99 - Dy/Fe multilayers 91-94 - Tb/Fe multilayers 101, 114 competitive interactions 407, 409, 429, 468, 469 compounds, ternary - with Cr 163, 233 - with Mn 233 - with Mo 233 - with Re 240 - with Si 207 - with Ti 210 – with V 222 - with W 240 concentration quenching 565 configuration diagram 545 configuration interaction (CI) 613, 630 conical spin structure 176 continuum dissolution 636 contribution of the conduction electrons 210 contribution of the uranium atom to the magnetic order 195 cooperative effects 557, 558, 560 - two-center transition 558 copper oxides 420, 471-483 see also rare-earth cuprates Coulomb interaction 630 coupled-cluster methods 613 Cowan-Griffin Hamiltonian 638-640 $[((cp^*)_2Lu)_2C_6H_4]$ 703 $[((cp^*)_2R)_2C_6H_4]$ 703 $[((cp^*)_2Sc)_2C_6H_4]$ 703 (cp)₂LuX 703 critical amplitudes 424

critical concentration 458, 467, 469 critical exponents 422, 424, 468 - for DyES 425 - for LiHoF₄ 425 - for LiTbF₄ 425 - for TbF₃ 425 critical field 22 critical temperature 414, 473 - for BaR₂F₈ 411 - for Cs₂NaRCl₆ 412 - for Cs₂NaRF₆ 412 - for $Cs_2NaR(NO_2)_6$ 412 - for CsR(MoO₄)₂ 412 - for KR(MoO₄)₂ 411 - for LiRF₄ 411 - for RAIO₃ 410 - for R₃Al₅O₁₂ 410 - for RAsO₄ 411 - for RBa₂Cu₂NbO₈ 412 - for RBa₂Cu₃O_{6+x} 412, 472 - for RBa₂Cu₄O₈ 412 - for R₂Ba₄Cu₇O₁₅ 412 - for RBaO₃ 412 - for RBr3 411 - for R(BrO₃)₃:9H₂O 411 - for R(C₂H₅SO₄)₃:9H₂O 411 - for R(CF₃SO₃)₃:9H₂O 411 - for RCl3 411 - for RCl₃:6H₂O 411 - for RCoO₃ 410 - for R₂CuO₄ 412 - for RF₃ 411 - for R3Ga5O12 410 - for R₂GaSbO₇ 410 - for R₂Ge₂O₇ 410 - for R(NO₃)₃:6H₂O 411 - for RNbO₄ 410 - for RO₂ 412 - for R₂O₃ 410 - for ROCI 410 - for R(OH)3 411 - for R₂O₂S 410 - for R₂O₂Se 410 - for R₂O₂SO₄ 410 - for R₂O₂Te 410 - for RPO₄ 410 - for RPO₄(MoO₃)₁₂:30H₂O 412 - for R₂(SO₄)₃:8H₂O 411 - for R₂Sn₂O₇ 410 - for $R_2 Ti_2 O_7$ 410 - for RVO₄ 410 $- for R_2 Zr_2 O_7$ 410 - for RbR(MoO₄)₂ 412 cross-relaxation 555, 564

- diffusion process 555 - self-quenching 555 cross-section 540, 542, 574 crystal field, see CEF crystalline electric field, see CEF crystallographic data - for crystals with zircon structure 304, 305 - for elpasolites 306 - for ethylsulfates $R(C_2H_5SO_4)_3 \cdot 9H_2O$ 301 - for LiRF₄ 303 - for RBa₂Cu₃O_{6+x} 472, 473, 482 - for RES 302 - for RF₃ 304 - for ThMn₁₂-type compounds 151-157, 161, 164-167, 170-174, 177, 179-181, 186, 189, 192-194, 196, 204, 205, 208, 209, 211-214, 216-219, 223-227, 232, 235-237, 241, 242, 262, 263 - for YES 303 Cs₂KRF₆ 306 Cs₂NaDyCl₆ 417 Cs₂NaErCl₆ 417 Cs₂NaErF₆ 305 Cs₂NaHoCl₆ 298, 318, 390, 392, 401, 414 Cs₂NaHoF₆ 305 Cs₂NaLnCl₆ 574 Cs₂NaPrCl₆ 363 Cs₂NaRBr₆ 306 Cs₂NaRCl₆ 306 Cs₂NaR(NO₂)₆ 408, 417 Cs₂NaTbCl₆ 363, 364 Cs₂NaYF₆ 305 Cu₅Al₇ 189 DOS (density of states) of ThMn₁₂ compounds 254-261 - calculated 258 - local 261 - spin-polarized 254, 255 - total 256 damping of Rabi oscillation by spontaneous decay 522 Davydov splitting 300, 366 de Gennes factor 8, 10 - effective 10 Debye temperature of R-doped silica and fluoride glasses 578 demagnetization factors of nonmetallic compounds 331, 402 demagnetizing field of nonmetallic compounds 402, 432 density-functional methods 613, 640 di- π -phthalocyaninecerium(III) 695

780

dielectric compounds, magnetic properties 295-492 differential efficiency of lasers 541 dilute crystals 457 diode pumping of lasers 580, 591 dipole-dipole energy transfers 531 Dirac-Coulomb-(Breit/Gaunt) Hamiltonian 613 Dirac-Hartree-Fock-Roothaan (DHFR) calculations 630 Dirac-Hartree-Fock-Slater method 641 Dirac-Hartree-Fock method 613, 632 Dirac equation 615 Dirac Hamiltonian 630 – unboundedness 632 Dirac matrices 631 displacement tensor of ions 308, 327 distribution of atoms in the 8(f), 8(i) and 8(j) positions of the ThMn₁₂ structure 151 domain - bubble phase in LiHoF₄ 404 - diffraction in LiTbF₄ 404 - in copper oxides 473, 474 - needle-like, in LiRF₄ 403 - relaxation rate, in LiTbF₄ 405 - stripe, in LiHoF₄ 404 - structure $- - in UCo_{10}Si_2 246$ - - in UFe_{10 - r}Ni_rSi₂ 247 - - in UFe10Si2 246 - wall energy - - in DyEs 403 - - in UFe₁₀Si₂ 267 - width - - in DyES 403 – – in LiHoF₄ 404 double fluorides, see tetrafluorides, LiRF4 Douglas-Kroll-Hess Hamiltonian 613, 636 Dy, see Dy film Dy-Co-Ga 154 Dy--Co--Ga system 206 Dy-Fe-Al 154 Dy-Fe-Ga 154 Dy-Fe-Re 157 DyAsO₄ 345, 419, 427, 458 DyBa₂Cu₃O₇ 318, 323, 421 DyBa₂Cu₄O₈ 421 Dy2Ba4Cu7O15 421 Dy(BrO₃)₃:9H₂O 418 DyCo10Mo2 236 Dy103Co10Mo194 236 DyCo₁₁Ti 216 DyCo₁₀V₂ 222, 229, 231, 247 DyCo_{12-x}V_x 227 DyCr₄Al₈ 164

DyCr₆Al₆ 190, 191 DyCu₄Al₈ 179 DyCu₆Al₆ 195, 196 DyES (dysprosium ethylsulfate) 299, 302, 318, 323, 405, 407, 417, 418, 424, 439, 441, 442, 448, 449, 452 DyFe₄Al₈ 169, 171, 172, 176 DyFe5Al7 186-188 - Mössbauer experiments 187, 188 - neutron diffraction 187, 188 time-dependent effects 188 DyFe₆Al₆ 193 $DyFe_{11-v}Co_vTi_x = 218$ DyFe₂Co₈V₂ 222 $DyFe_{10-x}Co_xV_2$ 230, 231, 252 $DyFe_{10-x}Co_{12-x}V_x = 227$ DyFe₁₀Cr₂ 232, 250, 251 DyFe_xGa_{12-x} 204 DyFe₁₀Mo₂ 250 $DyFe_{12-x}Mo_x$ 236 $DyFe_{12-x}Re_2$ 242 DyFe₁₀Si₂ 208 DyFe₁₁Ti 248, 250 $DyFe_{12-x}Ti_x$ 213 $DyFe_{11}TiC_{1-x}$ 262 $DyFe_{12-x}V_x$ 225 Dy film 5, 11, 12, 21, 29, 33, 36, 37 – *b*-axis 27 - on Lu, enhanced $T_{\rm C}$ 12, 22 - suppression of ferromagnetism 21 Dy_{1-x}Gd_xFe₁₁Ti 251 Dy/Lu superlattice 22, 42 - enhanced T_C 59, 61 - magnetic coherence length 61, 62 - magnetic structure 59, 63 - magnetoelastic domains 62 – turn angle 60 - X-ray diffraction 40, 45 DyMn₁₂ 158 DyMn₄Al₈ 167 DyMn₆Al₆ 190 DyOCl 420 Dy(OH)₃ 417 Dy2O2SO4 345, 418 DyPO₄ 345, 419, 458 DyTi_{1.1}Fe_{10.9} 220 DyVO₄ 305, 319, 345, 419, 427, 429, 458, 466 Dy/YDy superlattice 65 Dy/Y superlattice 4, 39, 48, 55 -a- and b-axis grown 28, 66–68 - field-induced transitions 52 - magnetic coherence length 50 - magnetic moment 49, 51 - magnetic structure 59

SUBJECT INDEX

Dy/Y superlattice (cont'd) - suppressed T_C 48, 49 - turn angle 48, 50, 61 DyZn₁₂ 161 Dy/Zr superlattice 64 EDFA (erbium-doped fiber amplifiers) 580, 587 – saturation power 587 - undersea experiment 587 EPR (electron paramagnetic resonance) 343, 425, 432, 433 see also Van Vleck paramagnets - in DyPO₄:Er, Yb 445 - in lanthanide nicotinate dihydrates 444 - in LiHoF₄ 444 - in LiTbF₄ 444 - in rare-earth cuprates 475, 479, 480, 483 - in Van Vleck paramagnets 387, 390 ES, see ethylsulfates ESA (excited state absorption) 560 effective core potentials 642-648 effective Hamiltonian 329, 331, 332, 340, 460 effective homogeneous linewidth 574 effective moments of the Fe atoms in RFe₄Al₈ 175 Einstein A coefficient 522 elastic compliancy 335 elastic constants 339, 353, 358 - for HoVO₄ 358 - for LiTmF₄ 351 - for LuAsO₄ 351 - for LuPO₄ 351 - for RVO₄ 351 - isothermic 335 - temperature softening 354 elastic energy 311, 334, 338 electric dipole moment 308, 425, 427 electric dipole operator 515 electric field effects 425-428 - in DyAsO₄ 427, 428 - in DyVO₄ 427, 428 - in LiHoF₄ 426, 427 - in Pr compounds 428 electric resistivity of ThMn₁₂-type compounds 160, 161, 176, 178, 195 electroluminescence spectra of GaAs:Er diode 596 electron correlation effects 609, 614, 619 - bond energies 622 - excitation energies 618 ionization potentials 618 electron paramagnetic resonance, see EPR electron-deformation interaction 310, 327, 337 - effects

- - on temperature behavior of elastic constants 335, 351, 353, 354, 434, 435, 439 - on thermal expansion 337, 350 - for Er^{3+} :LiLuF₄ 339 - for Er³⁺:LiTmF₄ 339 - for Er³⁺:LiYF₄ 339 - for HoVO₄ 359 - for YVO_4 :Tm³⁺ 339 - renormalized constants of coupling with macroscopic strains 337, 340, 359 electron-nuclear magnetism 414 electron-phonon interaction 309, 326 electron-rotation interaction 310, 333, 334, 358 electronic structure - calculations 609 - - for lanthanide molecules 607-718 - for ThMn₁₂-type compounds 160, 257, 258 - of ThMn₁₂-type compounds 254 electronic transitions in two-level atom, induced and spontaneous 512 elemental semiconductors doped with Er³⁺ 594 elpasolites, A2BRX₆ 305, 409 energy levels 318, 321 - in Cs₂NaHoCl₆ 318 - in DyBa₂Cu₃O₇ 318 - in DyES 318 - in DyVO₄ 319 - in ErBa₂Cu₃O₇ 318 - in HoAsO₄ 319 - in HoBa₂Cu₃O₇ 318 - in HoES 319 - in HoPO₄ 319 - in HoVO₄ 318 - in LiDyF₄ 318 - in LiErF₄ 318 - in LiHoF₄ 319 - in LiTbF₄ 319 - in LiTmF₄ 318, 398 - in LiTmF₄:Nd³⁺ 399 - in TbAsO₄ 319 - in TbES 319 - in TbPO₄ 319 - in TbVO₄ 319 - in TmAsO₄ 319 - in TmBa₂Cu₃O_{6+x} 318 - in TmBa₂Cu₃O_{6.5} 318 - in TmBa₂Cu₄O₈ 318 – in TmES 318 – in TmPO₄ 318 - in TmVO₄ 319 - in YbBa2Cu3O7 318 energy product for RFe_{~6}Ga_{~6} 202 energy transfers in R-doped lasers 549, 556 - activator 549

782

- critical activator concentration 554 - critical R_0 551 - diffusion-limited 555 - diffusion rate 554 - electric multipolar interactions 551 - fast diffusion 555, 569 - index of the multipolar interaction 554 - inhomogeneous broadening 553 - limited diffusion 569 - macroscopic samples 553 - magnetostatic and exchange interactions 551 - microscopic case 553 - multiphonon phenomena 552 - multiphonon sidebands 552 - multipolar interactions 551 - nonradiative 549 - overlap 550 - overlap integral 551, 553 - phonon-assisted 549, 552 - radiative 549 - rapid energy migration 554 - resonant 549 - sensitizer 549 enhanced electronic specific heat constant in CeCu₄Al₈ 182 enhanced NMR in $TmBa_2Cu_3O_{6+x}$ 479 see also nuclear magnetic resonance enhanced nuclear magnetism - non-Kramers ion 409 - Tm³⁺ ions 346 – – LiTmF₄ 346 -- TmES 346 epitaxial growth of CaF₂:Er³⁺ layers 600 epitaxial waveguide lasers 600 - Nd³⁺:YAG 600 - Yb³⁺:Er³⁺:YAG 600 – Yb³⁺:YAG 600 epitaxy of metallic nanostructures 3-39 - anelastic response 5, 19, 26, 27 - bcc metals on sapphire 15, 16, 19 - buffer layer 14, 16 - clamping 7, 14, 20, 22, 72 - coherency strain 5-7, 14, 19-22, 26, 59, 72 - epitaxial phase diagram 21-23, 27, 56, 61 - growth 14-19, 71 - hcp metals on sapphire 15-17 - magnetism 19-39 - metal substrate 17 - mica substrate 18, 35 - pseudomorphic growth 5, 22, 27, 32 - tilted 19, 20, 71 Er³⁺ - doped glass fibers 592

 doped silica-based planar waveguides on silicon substrate 599 – doped ZBLAN 588 - implanted in Si, GaAs, GaP, InP 594 - in fluorides 531 - in silica glass 587 – ZBLAN 537 Er. see Er film Er-Fe-Al 154 Er-Fe-Ga 154 Er-Mn-Ga 154 ErBa2Cu3O6 323 $ErBa_2Cu_3O_{6+x}$ 422 ErBa₂Cu₃O₇ 318, 323 ErCl₃·6H₂O 424 ErCo10Mo2 237, 238 ErCo10.5 Mo1.5 252 Er_{1.03}Co₁₀Mo_{1.94} 237 ErCo₁₁Ti 216 ErCo10V2 229 $ErCo_{12-x}V_x = 227$ ErCr₄Al₈ 164 ErCr₆Al₆ 190, 191 ErCu₄Al₈ 179 196 ErCu₆Al₆ ErES (erbium ethylsulfate) 302 Er(Fe, Co)10.4 Mo1.5 247 $ErFe_xAl_{12-x}$ 199, 200 ErFe₄Al₈ 173 ErFe₅Al₇ 185-188 Mössbauer experiments 187, 188 - neutron diffraction 187, 188 time-dependent effects 188 ErFe₆Al₆ 193 ErFe5.5Co5.0Mo1.5 238 $ErFe_{10.5-x}Co_xMo_{1.5}$ 237, 252 $ErFe_{10.5-x}Co_xMo_2$ 239 ErFe₁₀Cr₂ 232, 253 ErFe_xGa_{12-x} 205 $ErFe_{12-x}M_x = 250$ ErFe₁₀Mo₂ 250 ErFe_{10.5}Mo_{1.5} 252 ErFe_{12-x}Mo_x 236 $ErFe_{12-x}Re_2$ 242 ErFe₁₀Si₂ 209 ErFe₁₁Ti 245 $ErFe_{12-x}Ti_x$ 214 $ErFe_{11}TiC_{1-x}$ 262 ErFe_{9.25}V_{2.75} 248 ErFe₁₀V₂ 245, 246, 248 $ErFe_{12-x}V_x$ 226, 229 Er film 5, 12, 24, 25, 28, 30, 36, 37, 55 - critical field 28, 29, 58, 59 - neutron scattering 13, 28, 31

SUBJECT INDEX

ErMn₁₂ 158 ErMn₄Al₈ 167 Er₂O₃ 420 $(Er_{0.5}Sm_{0.5})Fe_{11-x}Co_xTi 219$ Er/Y superlattice 42, 54, 55 - critical field 59 - field-induced transitions 57 - magnetic moment 57 - turn angles 55-57 ErZn12 161 - specific heat 162 ethylsulfates, R(CH₂H₅SO₄)₃9H₂O (RES) 301, 325, 343, 406, 409, 416 Eu₂ 681 Eu-Mn-Al 154 EuCl₃.6H₂O 391 EuCu₄Al₈ 179, 182 EuES (europium ethylsulfate) 390, 391 EuF 677 EuF_o⁶⁻ 715 EuFe₄Al₈ 171, 175 EuFe₆Al₆ 190, 194, 195 Eu₃Ga₅O₁₂ 390, 392 EuH 657 EuMn₄Al₈ 166, 168 EuO 670 - electronic states 670, 672 - population analysis 671 - spectroscopic constants 670 -EuO₆⁹⁻ 706 - electronic states 708 - spectrum 709 Eu(OH)₃ 391 EuPO₄ 391 Eu₂(SO₄)₃·8H₂O 391 [Eu(acac)₃o-phen] 705 Eu@C₆₀ 697 Eu@C⁺₆₀ 697 Ewald method in dielectric compounds 315, 328, 403 exchange - charge in dielectric compounds 317, 325, 327, 328, 338, 399, 464 - correlation potential for $YFe_{12-x}Mo_x = 258$ - coupling constant for U ThMn₁₂-type compounds 185 - energy in ThMn₁₂-type compounds 261 - field in dielectric compounds 402, 432, 445 - integral in dielectric compounds 343, 420, 432 - interaction in metallic nanostructures 6 -- Heisenberg 6, 7 - - indirect 5, 7, 50, 73-76 - - interlayer 7, 48, 67, 69-72

- - intralayer 6 - - s-f 7, 9, 76 - interaction in ThMn₁₂-type compounds 244, 252 - - anisotropy 243 exponential laws 544 extended Hückel method 613 5f-ligand hybridization 185 FOMP, see first-order magnetization process Fe₅Al₇ 189 Fe10Si2 209 Fe₃Sm 266 Fermi energy in ThMn₁₂-type compounds 254-256, 260 Fermi surface in metallic nanostructures – gaps 6 - nesting 6, 69 - superlattice 70 ferromagnetic transition in metallic nanostructures 14 - enhanced T_C 22, 59, 73 suppression of 21, 24, 48 ferromagnets, dielectric compounds - canted 410-412, 415, 419, 424 - dipolar 403, 404, 430, 468 - uniaxial 425, 468 field-coupled cooperative multi-ion effects 524 see also superradiance and superfluorescence field-induced phase transition, see metamagnetic transition figure of merit for lasers - 3-level case 581 - KNdP₄O₁₂ (KNP) 566 - LiNdP4O12 (LNP) 566 - material 541 - Na2Nd2Pb6(PO4)Cl2 (CLAP) 566 - Na₅Nd(WO₄)₄ 566 - NdAl₃(BO₃)₄ (NAB) 566 - NdP5O14 (NdUP) 566 - NdTa₇O₁₉ 566 powdered samples luminescence method 565 - YAG:1%Nd 566 film, epitaxial 4 see also thin films - epitaxial crystal limit 29 - interfacial limit 20, 32-34, 72 - thick limit 20, 25, 26 finite basis set disease 635 finite nucleus model 631 first-order magnetization process (FOMP) 210, 213, 237, 238, 270 fluorescence line-narrowing 553

fluoride glasses 585, 590

784
fluorophosphate glasses 577 fluorozirconate glass (ZBLAN) 585 Foldy-Wouthuysen transformation (FWT) 636 free induction decay 526 free induction emission 517 Fresnel number 529 fullerene complexes 695-700 GaAs, AlGaAs, and GaAs/AlGaAs quantum wells 594 GaAs:Er 594 GaAs:Er³⁺ diode structure 596 GalnAsP diode active layer with Er³⁺ 597 gain flatness in fluoride glasses 588 gallides 154, 202-206 garnets, R₃M₅O₁₂ 301, 408 Gaunt term 632 GdAlO₃ 345, 468 GdAsO4 305, 344, 419 Gd10C4Cl18 705 GdCl₃ 344 GdCo10Mo2 236 Gd_{1.03}Co₁₀Mo_{1.94} 236 GdCo11Ti 216 GdCo_{12-x}V_x 227 GdCr₄Al₈ 164 - ⁵⁵Gd Mössbauer experiment 163 - magnetization 163 GdCr₆Al₆ 190, 191 GdCu₄Al₈ 179, 182 GdCu₆Al₆ 195, 196 Gd₂ dimer 680 Gd/Dy superlattice 65 GdF₈⁵⁻ 706 GdFe₁₂ 160, 161, 257 $GdFe_xAl_{12-x}$ 197 GdFe₄Al₈ 169, 171, 175 GdFe5Al7 186-188 GdFe₆Al₆ 192 GdFe₁₀Al₂ 198 $GdFe_{11-y}Co_yTi_x$ 217 GdFe₁₀Cr₂ 232 GdFe_xGa_{12-x} 204, 206 GdFe_{12-x}Mo_x 235 $GdFe_{12-x}Re_2$ 242 GdFe10Si2 157, 208, 268 $GdFe_{12-r}Ti_r$ 212 $GdFe_{11}TiC_{1-x}$ 262 $GdFe_{12-x}V_x = 225$ GdFe_{10.8}W_{1.2} 246 $GdFe_{12-x}W_x = 241$ Gd film 18, 20, 34, 36, 37 - 2D limit 18, 36 GdMn₁₂ 149, 158, 160

GdMn₄Al₈ 166, 168 GdMn₆Al₆ 190 Gd17NdO3(MoO4)3 573 GdO 663, 666 - electronic states 666 - population analysis 667 - spectroscopic constants 666 - spin density 667 Gd(OH)₃ 344 Gd₂O₂SO₄ 418 GdRh₆Al₆ 195, 197 GdVO₄ 344, 419, 445, 458 $Gd_{1-x}Y_{x}Mn_{12}$ system 158 - Néel point 159 - saturation magnetic moment 159 Gd/Y superlattice 39, 47 -a- and b-axis grown 68, 69 - coercive fields 48 - magnetic structure 47, 48 GdZn₁₂ 161 - electric resistivity 162 Ginzburg criterion 423 glass ceramics 578, 599 glass fibres 582 - absorption 583 - emission 583 - radiative energy transfer 584 - single-mode condition 582 - transmission properties 582 glasses 556, 562, 567, 569, 578 - harmonic generation 579 Hartree-Fock - energy 260 - method 613, 632 - radial integrals 243 Hartree-Fock-Slater method 641 heavy-fermion-like behavior in ThMn12-type compounds 286 heavy fluoride glasses doped with Er^{3+} , Pr^{3+} , Tm³⁺ 588 Heisenberg model for dielectric compounds 343, 419 hexachlorides, A2BRCl6 364 see also elpasolites high-power laser 577 peak power 579 Ho³⁺ - doped fluoride fiber laser 592 in fluorides 531 Ho, see Ho film Ho-Cu-Al 154 Ho-Cu-Ga 154 Ho-Fe-Al 154

SUBJECT INDEX

Ho-Fe-Ga 154 HoAlO₃ 414 Ho3Al5O12 415 HoAsO₄ 305, 319, 345, 419 HoBa₂Cu₃O₇ 318, 323, 422 HoCo10Mo2 237 Ho1.03Co10Mo1.94 236 HoCo₁₁Ti 216 HoCo10V2 229 HoCr₄Al₈ 164 HoCu₄Al₈ 179 HoCu₆Al₆ 196 HoES (holmium ethylsulfate) 319, 323, 417 Ho/Er superlattice 65 HoF₃ 305, 415 HoFe₄Al₈ 169, 172, 173, 176 HoFe₅Al₇ 186, 187 HoFe₆Al₆ 193 $HoFe_{10-x}Co_xMo_2$ 237 HoFe_{11-v}Co_vTi_x 218 HoFe₁₀Cr₂ 232, 249 HoFerGa12-r 204 HoFe10Mo2 248, 249 HoFe_{12-x}Mo_x 236 $HoFe_{12-x}Re_2$ 242 HoFe10Si2 208, 249 HoFe₁₁Ti 248, 249 HoFe_{12-r}Ti_r 214 $HoFe_{11}TiC_{1-x}$ 262 HoFe10V2 249 $HoFe_{12-x}V_x = 226$ Ho film 25 - spin slip 25 Ho/Lu superlattice 63 HoMn₁₂ 158 HoMn₄Al₈ 167 Ho(OH)3 417 Ho₂O₂SO₄ 345, 418 HoPO₄ 319, 322, 345, 419 HoTi_{1.1}Fe_{10.9} 220 HoVO₄ 305, 318, 322, 351, 354, 357, 358, 387, 400, 401, 414 Ho/Y superlattice 54 - spin-slip structure 54 - turn angles 54 HoZn₁₂ 161 Huang-Rhys electron-phonon coupling parameter 545-548 hybridization in ThMn₁₂-type compounds 259, 286 - interactions 182 hydroxides, R(OH)₃ 416

hyperfine interaction in dielectric compounds 307, 310, 346, 348, 367, 417, 426, 429, 443, 450, 469, 484 hypersensitive transitions in lasers 542 hypothetical YFe₁₂ magnetic moment 149 hysteresis loops in ThMn₁₂-type compounds 199 InGaAs-diode-pumped Er³⁺:ZBLAN fiber 592 InGaAsP laser 598 InP:Yb 597 integrated cross-section - Ca10(PO4)F2 (5FAP) 575 - Nd₂P₅O₁₄ (NdUP) 575 - Y₃Al₅O₁₂ (YAG) 575 interactions between Ln3+ ions - dipole-dipole 344 - - magnetic 311, 330, 342, 409, 423, 485 - electric multipole 342 - exchange 311, 331, 342, 409 - - parameters for Er:Tb(OH)₃ 343 - non-dipole 344 - via the phonon field 311, 331, 343, 361, 456 - - tensor of constants 352 interface anisotropy 105 - determination of 105, 106 - on Dy/Co multilayers 106 - on DyNi/Mo multilayers 106 - on Nd/Fe multilayers 106 - on Tb/Co multilavers 106 interfacial magnetism of rare-earth-transition-metal multilayers 85, 86, 111, 114-116, 139 see also Mössbauer effect - determination of R-T exchange coupling 135 - determined by MCXD 108-113 - interface anisotropy. see interface anisotropy - magnetic interaction 85, 87, 88, 139 see also perpendicular magnetic anisotropy (PMA) magnetic structure 86–88, 117 intermediate neglect of differential overlap method 613, 648-650 internal deformation of dielectric compounds 356, 432 see also sublattice displacements interstitial nitride, carbide 266 ion-ion energy transfers 531 ionic model 651 Ising antiferromagnets 419, 421, 458 Ising ferromagnets 299, 403, 419, 423, 424, 426, 435, 437 Ising model, transverse 409, 417 Jahn-Teller ferroelastics 299, 319, 367, 409-412, 427, 429, 458

- self-consistent field constants for vanadates 463.464 - structural phase transition stimulated by a magnetic field 361 - tensor of multipole-multipole interactions in RMO₄ 353 Judd's theory 542, 575 $-\Omega_{\lambda}$ 543 $-T_{\lambda}$ 542 KDy(MoO₄)₂ 429 $K[Ln(C_8H_8)_2] = 689$ K₃Nd(PO₄)₂(KNP) 569 K₃Nd(WO₄)₄ 573 KY₃F₁₀ 573 KYF₄:Er³⁺ 591 KY(MoO₄)₂ 573 Kondo effect 692 Kondo system, CeCu₄Al₈ 178 LMTO (linear-muffin-tin-orbitals) method 254, 255, 257, 258 - LMTO-ASA (atomic-sphere approximation) method 257, 258 LOS (Nd₂O₂S) 573 LSD (local-spin-density) approximation 258, 270 La-Mn-Al 154 LaAu 682 - spectroscopic constants 683 LaBr₃ 706 LaCo₁₁Ti 216 LaCr₄Al₈ 164 La₂ dimer 681 LaF 677 ${f LaF_3} {f 706} {f LaF_9} {f 715}$ LaF3:Nd 567 LaF₃:Pr³⁺ 531 LaFe₄Al₈ 170 LaH 655 LaH₃ 684 LaMn₄Al₈ 166 LaO 661, 663 LaO₄⁵⁻ 706 La2O3 573 LaOF 572 LaOF(Nd³⁺) 573 La@C₆₀ 697 La@C+ 697 La@C82 699 $La@C_{60}^{q}$ 697 lanthanide - contraction 222, 233, 624, 625

- dimers 680, 681 see also individual elements, e.g. Gd₂ - - binding energies 682 - ground state 612 - ions, hydrated 700-703 - monofluorides 677-680 - - binding energies 679 --- spectroscopic constants 678,680 - monohydrides 655-659 - - binding energies 657, 658 - - spectroscopic constants 656, 659 - monoxides - - binding energies 661 - - population analysis 665 - - spectroscopic constants 662, 667 - trifluorides, atomization energies 688 laser - 3-level 587 - 4-level 541 - cross-section 575 - - fluorophosphate glass LG 810 575 - - fluorozirconate glass (ZrF₄, BaF₂, LaF₃) 575 -- (LNA) LaMgAl11019 575 $- - (NdUP) Nd_2P_5O_{14} 575$ - - phosphate glass (P2O5, Na2O, K2O, CdO) 575 - - silicate glass LG 650 575 - - tellurite glass (TeO₂, Li₂O) 575 - - Y₃Al₅O₁₂ (YAG) 575 - diode pumping 584, 587, 599 - effect 540 - - threshold condition 540 - line strengths 574 - linewidth - - homogeneous 531 - - natural 520 - materials 564 - - figure of merit 564, 565 - – high-concentration Nd³⁺ 566 lattice deformation 309 macroscopic 332, 335 - microscopic 332, 335 - parameters 326, 332, 334 lattice parameters of ThMn12-type compounds 154-156, 160, 161, 164-167, 170-174, 177, 179-181, 186, 189, 192-194, 196, 204, 205, 208, 209, 211-214, 216-218, 220-227, 231-233, 235-242, 262, 263, 268, 269, 274, 276, 277, 280, 283 lattice sums 315, 406, 407 - for DyVO₄ 416 - for LiTbF₄ 416 - for RES 399 - for TbF₃ 416

layered structure in rare-earth-transition-metal multilayers 89 Leibfried-Schloemann formula 577 LiDyF₄ 318, 323, 341, 433, 434 LiErF₄ 318, 323, 341, 344, 433, 434 LiHoF₄ 319, 323, 344, 418, 419, 424, 426, 427, 434, 435 LiLuF₄ 350, 353 LiNbO₃ 573 LiNdNbO₄ 573 LiNd(PO₃)₄ 573 LiNdP₄O₁₂ (LNP) 566 LiRF₄ 302, 323–325, 338, 339, 350, 419, 433 LiTbF₄ 304, 319, 323, 344, 354, 404, 405, 415, 419, 424, 433, 435, 439 LiTmF₄ 300, 318, 323, 338, 350, 353, 355, 356, 362, 364, 388-390, 392, 393, 396-399 - longitudinal magnetostriction 356 Li(Y, Nd)F₄ 573 LiYF₄ 304, 434 532, 533, 591 LiYF₄:Er³⁺ LiYbF₄ 304 ligand field theory 614, 650 linewidth, see laser linewidth LnAg5.4In6.6 206 LnCO 703 LnP₅O₁₄:Tb³⁺ 570 local deformation 396, 462 - in LiTmF₄:Lu³⁺ 399 - in LiTmF₄:Nd³⁺ 399 - in TmVO₄:Lu³⁺ 461 - in TmVO₄:Tb 462 – in TmVO₄:Tb³⁺ 461 local magnetic field 331, 402, 483 - at ¹⁹F in LiTmF₄ 371 - at protons in TmES 370 - fluctuations 367, 456 $- - \text{ rate } \tau, \tau_c = 378, 456$ local moment of Fe in ThMn12-type compounds 257 longitudinal relaxation 453, 455 see also spin-lattice relaxation - mechanisms 379 - of ¹H in TbES and DyES 454 - protons in TbES and DyES 453 - rate T_1^{-1} 379, 455 Lorentz field in dielectric compounds 315, 331, 402 low-field electroluminescence of Er³⁺ 595 Lu-Cu-Al 154 LuAsO₄ 305 LuAu 682 - spectroscopic constants 683 LuC₈₂ 700

LuCo10Mo2 237 Lu_{1.03}Co₁₀Mo_{1.94} 237 LuCr₄Al₈ 164 LuCr₆Al₆ 191 LuCu₄Al₈ 180, 182 LuCu₆Al₆ 196 Lu₂ dimer 681 LuF 677 LuFe₄Al₈ 174 LuFe5Al7 186, 187 LuFe_{10-x}Al_xSi₂ 284, 285 LuFe₁₀Cr₂ 232 $LuFe_xGa_{12-x}$ 205 $LuFe_{12-x}Mo_x$ 236 $LuFe_{12-x}Re_2$ 242 LuFe₁₀Si₂ 207, 209 $LuFe_{12-x}Ti_x$ 214 $LuFe_{11}TiC_{1-x}$ 262 $LuFe_{12-x}V_x$ 226 LuH 655 LuMn₄Al₈ 167 LuO 661, 663 LuPO₄ 351 LuZn₁₂ 161 Luttinger-Tisza method 407, 421 MBE (molecular beam epitaxy) - GaAs:Er³⁺ 595 layers 594 MCSCF (multi-configuration self-consistent field) 635 ME, see Mössbauer effect MFA (molecular-field approximation, mean-field approximation) 252, 254 - in dielectric compounds 414, 415, 417, 423, 426, 430, 469 in ThMn₁₂-type compounds 253 $MMFe_xGa_{12-x}$ (MM = mischmetal) 204 MO-LCAO (molecular orbitals by linear combination of atomic orbitals) 635 MRCI (multi-reference configuration theory) 635 MRPT (multi-reference perturbation theory) 635 MS-LCAS (molecular spinors by linear combination of atomic spinors) 635 MVM, see magnetic valence model magnetic anisotropy 199, 276 magnetic circular X-ray dichroism measurements (MCXD) 89, 113 see also interfacial magnetism magnetic cooling, see nuclear magnetic cooling magnetic coupling in ThMn₁₂-type compounds 150 magnetic hysteresis in ThMn12-type compounds 185

magnetic order in metallic nanostructures - - c-axis modulated (CAM) 10, 14, 31, 54 - - effect of epitaxial strain 5, 30, 31 --- ferromagnetic 12, 22 - - field-induced 52 - - helical 10, 14, 55 - - lanthanide elements 4, 7, 10, 11 - - lutetium alloys 10, 25 - propagation through non-magnetic layers 4, 39.50 - - yttrium alloys 10 - in ThMn₁₂-type compounds 163, 182 magnetic ordering see also Néel temperature - in dielectric compounds 407, 458, 468 - - electron-nuclear regime 469 - - electronic regime 414, 469 – nuclear regime 414 magnetic phase diagram T(x, M) for ThMn₁₂-type compounds 252 magnetic properties see also coercivity, energy product, ferromagnetic transition, ferromagnets, hysteresis loops, and interfacial magnetism - of dielectric compounds 346-471 - of metallic nanostructures 10-14, 19-73 - of rare-earth-transition-metal multilayers 81 - 140 of ThMn₁₂-type compounds 157–286 - - ferrimagnetic order 188 - - ferrimagnetism 176, 200 - of Van Vleck paramagnets 346-402 magnetic structure - in dielectric compounds 407, 418-420, 422 - - in HoVO₄ 402 $- - \text{ in } RBa_2Cu_3O_{6+x}$ 421 - in ThMn₁₂-type compounds 149, 159, 178, 190 – – GdMn₁₂ 159 magnetic susceptibility 175, 178, 182 - Curie-Weiss temperature in LiRF₄ 403 - Curie constant in LiRF₄ 403 - Van Vleck 341, 347, 362, 372 magnetic transitions, see first-order magnetization process, magnetic ordering, metamagnetic transition, and Néel temperature magnetic valence 252, 259-261 - model 259, 260 magnetism in ThMn₁₂-type compounds, contribution of f-electron element 195 magnetization - in dielectric compounds 336, 349, 386, 422 - - easy axis 403, 471 - - easy plane 408

- - electronic 331, 347 - - for TmPO₄ 359 - - nuclear 347 - - saturation 439 -- spontaneous 404, 430, 435 - in rare-earth-transition-metal multilayers -- compensation point 91, 96, 101 - - distribution in multilayers 116, 117 - - layer-thickness dependence - - - for Dy/Co multilayers 96 - - - for Dy/Fe multilayers 91-94 - - - for Tb/Fe multilayers 101-103 - - orientation of magnetic moments in multilayers 136-138 - - temperature dependence - - - for Dy/Co multilayers 99, 100 - - - for Dy/Fe multilayers 94, 95 - - - for Tb/Fe multilayers 101-105 - - total and subnetwork magnetizations 116, 117 - in ThMn₁₂ compounds, negative 199 magnetization reversal in rare-earth-transitionmetal multilayers 86, 125, 140 - micromagnetic calculation 132, 133 - model of 130-132 on Dy/Fe multilayers 128–130 - on Tb/Fe multilayers 126-128 magnetocrystalline anisotropy in ThMn12-type compounds 257 - energy 284 - total 284 magnetoelastic domains in metallic nanostructures 22-24, 62 magnetoelastic effects in dielectric compounds 329, 332, 428 - changes of acoustic wave velocity in a magnetic field 357, 358, 435, 439 - - in LiTbF₄ 439 $-\Delta E$ -effect 361 - two-particle mechanism of 332, 335, 430, 436 magnetostriction - in dielectric compounds 336 - - induced (forced) 360, 361, 429, 437 see also parastriction - - - sample shape dependence 433, 438 - - longitudinal 355, 432, 434, 436 - - - dipolar ferromagnets 436 --- in LiTbF₄ 436-438 --- in LiTmF₄ 355 --- in TmPO₄ 355 -- optical detection of 356 -- spontaneous 336, 408, 434 -- transverse 355

-- in LiTmF₄ and TmPO₄ 355

magnetostriction (cont'd) - in metallic nanostructures 3, 13, 14, 20, 22-24, 37, 54, 59, 61 - in ThMn₁₂-type compounds 195 many-body perturbation theory 635 marginal dimensionality 423 materials for CW lasers 565 maximum ground-state splitting of ${}^{4}I_{9/2}(Nd^{3+})$ and crystal-field strength 573 maximum phonon frequency in lasers 544, 578 M(cp*)₂ 690 mean-field approximation, see MFA mechanical alloying 264-266 Melamed's theory 567 melt-spinning 265 metamagnetic transition - in dielectric compounds 416, 418 in ThMn₁₂-type compounds 270 microchip-type laser 567, 599 Miller rule 579 M@C₂₈ 696 - structure 696, 697 M@C₆₀ 697 - structure 698 M@C⁺₆₀ 697 mischmetal ThMn₁₂-type compounds 206 mixed crystals (solid solutions) of dielectric compounds 457 - dispersion of Stark splittings 463 mixed valence behavior in ThMn₁₂-type compounds 163, 175, 182, 202, 234, 286 Mn₅Al₇ 189 mode-locking processes in lasers 579 mode selection of an InGaAsP laser by Er³⁺ absorption 598 model potentials 642-648 molecular field - in dielectric compounds 299, 331, 332, 405-407, 443 - - at protons in TbES and DyES 441 --- constants 362, 432 - - transient processes in 445 - in ThMn₁₂-type compounds 253 molecular-field approximation, see MFA Møller-Plesset perturbation theory 613, 635 monoxides 660-676 Monte-Carlo simulation 418, 421 Mössbauer effect - Fe moment orientation - - in Dy/Fe 113 - - in Nd/Fe 113 - - in Tb/Fe 109 - in rare-earth-transition-metal multilayers 89, 108-113

- in ThMn₁₂-type compounds 168, 169, 175, 176, 182, 185, 188, 190, 195, 198, 202, 203 - - experiments 202 --- (R,An)Fe₄Al₈ 169 --- RMn₄Al₈ 168 - - hyperfine field 190 - - investigations 190 - - results 202 - - spectra 198, 200 - interfacial magnetism determined by 108-113 multilayer see also superlattice - R/transition metal 81-140 multiphonon - assisted pumping 592 - decays 531 - nonradiative processes 568 – order 576 - processes 544 - - accepting modes 546 - - exponential parameter α_s 544, 576 - - M and Δ processes 546 multipole - expansion method 614 - polarizabilities 317, 324 NA, see numerical aperture ND, see neutron scattering *n*-photon summation 559, 560 Na0.5Gd0.5WO4:Nd 567 Na(La, Nd)(WO₄)₂ 573 $NaLn(WO_4)_2:Tb^{3+}$ 570 Na₁₈Nd(BO₃)₇ 573 NaZn₁₃-type structure 207, 208 Nd^{3+} - - doped lithium niobate optical waveguide 599 - spectral overlap integral – for diffusion $- - Na_2Nd_2Pb(PO_4)Cl_2$ (CLAP) 569 $- - - NdNa(WO_4)_2$ 569 --- NdP₅O₁₄ (NdP.P) 569 --- YAG:Nd 569 - - for quenching ---- Na2Nd2Pb(PO4)Cl2 (CLAP) 569 $- - - NdNa(WO_4)_2$ 569 --- NdP₅O₁₄ (NdP.P) 569 --- YAG:Nd 569 Nd, see Nd film (Nd, La)F₃ 573 (Nd, Y)Fe11 Ti 251 Nd,YFe_{12-x}Ti_x 211 Nd-Co-Mn 156 Nd-Cu-Al 147 Nd-Fe-Al 154

Nd-Fe-B derivatives 264 Nd-Fe-B systems 207, 266 Nd-Fe-Ga 154 Nd-Fe-Mo 147 Nd-Mn-Ni 156 Nd-Ti-Fe 264 NdAl₃(BO₄)₃ 573 NdBa2Cu3O7 421 Nd(C₂H₅ZO₄)₃.9H₂O 573 Nd(CO)_n 703 NdCl₃ 344, 417, 538, 572, 573 NdCl₃:6H₂O powder 538, 539 NdCo10Cr2 258 NdCo10Mo2 236, 237 NdCo10.2 Mo1.8 252 NdCo11Ti 216 NdCo10V2 258 $NdCo_{12-x}V_x$ 227 NdCr₄Al₈ 164 NdCu₄Al₈ 179 $Nd_rDy_{1-r}Fe_{10}Ti = 265$ $NdF_3 706$ $NdF_8^{5-} 706$ Nd(Fe, Co)_{10.2}Mo_{1.8} 252 NdFe₄Al₈ 170 Nd₂Fe₁₄B 263, 267 NdFe_{10.2-x}Co_xMo_{1.8} 237, 238 $NdFe_{11-v}Co_vTi_x$ 217 $Nd(Fe_{10-x}Co_x)V_2 = 227$ NdFe₁₀Cr₂ 232 NdFe10Cr2-Nd0.67B0.33 263 $NdFe_xGa_{12-x}$ 204 NdFe10Mn2 233 $NdFe_{12}$ Mn_r 233 NdFe_{12-x}Mo_x 235 Nd₈Fe₈₂Mo₁₀ 265 NdFe₁₀Re₂ 242 $NdFe_{12} - Re_2 = 242$ NdFe10Si2 208, 247 NdFe₁₁Ti 258 $NdFe_{12-x}Ti_x = 211$ $NdFe_{11}TiC_{1-x}$ 262 NdFe₁₁TiN_x 258 NdFe_{12-x}V_x 224, 229, 230, 234, 251 Nd film 14, 25 $[Nd(H_2O)_n]^{3+}$ 702 NdLaPP 569 NdMn₄Al₈ 166 5Nd(MoO₄)₄ 573 NdNb5O14 573 Nd₅Nd(WO₄)₄ 573 Nd(OH)₃ 344, 417 NdP5O14 573 NdP₅O₁₄ (NdUP or NDPP) 567

Nd₂S₂ 573 Nd/Y superlattice 65 Néel temperature of dielectric compounds 420, 422, 434, 445, 471 neutron scattering - by metallic nanostructures - - cross section 10, 40 - - diffusion model 44 - - Dy film 11 - - Er film 11 - - magnetic satellites 11, 12, 41 - - rectangular model 40, 41 - - superlattice harmonics 40 - by ThMn₁₂-type compounds 157, 168, 169, 176, 178, 182, 183, 185, 188, 195, 201 – – polarized 178 nitrides, $Sm_x Fe_v N_z = 266$ nonmetallic compounds, magnetic properties 295-492 nonradiative transitions in lasers 544-546 nonadiabatic Hamiltonian method 545 - Nth-order perturbation method 545 NpCr₄Al_{8-x} 163 NpCr₄Al₈ 165 NpCu₄Al₈ 181, 182 NpFe₄Al₈ 177, 178 NpFe₅Al₇ 189, 202 nuclear acoustic resonance 377, 386 nuclear magnetic cooling 399 nuclear magnetic ordering 401, 469 nuclear magnetic resonance (NMR) of dielectric compounds - effects of thermal excitations of Ln³⁺ ions 377 - in magnetically-concentrated systems 405, 439 - lineshape 373, 448, 449 - - mechanisms of line broadening 373, 377, 448 - - second moment 374, 376, 450 - of ¹³³Cs in Cs₂NaHoCl₆ 373 - of ¹⁹F 443 - - in LiHoF₄ 443 -- in LiTbF₄ 443 $- - in LiTmF_4$ 371, 372 - of ^{1}H - - in DyES 442 -- in TmES 370, 372 - of ¹⁶⁵Ho - - in Cs₂NaHoCl₆ 366, 367 - - in Cs₂NaHoF₆ 367 - - in HoF₃ 363, 367 - - in HoND 367 - - in HoVO₄ 363, 366 -- in Rb₂NaHoF₆ 363, 367

nuclear magnetic resonance (NMR) of dielectric compounds (cont'd) – of ⁷Li - - in LiHoF₄ 443 - - in LiTbF₄ 443 - of ²³Na in Cs₂NaHoCl₆ 372, 373 - of ³¹P in TmPO₄ 372 - of 141 Pr - - in Cs₂NaPrCl₆ 363 -- in PrAlO₃ 363, 365 -- in PrF₃ 363 $- - in Pr(NO_3)_3:6H_2O = 363$ - - in Pr₂(SO₄)₃:8H₂O 363 -- in PrVO₄ 363 - of ¹⁵⁹Tb in Cs₂NaTbCl₆ 363 - of ¹⁶⁹Tm - -- in Cs₂NaTmCl₆ 363 -- in LiTmF₄ 361, 363 $- - in Tm_3Al_5O_{12}$ 363 $- - in TmAsO_4$ 363 $- - in TmBa_2Cu_3O_{6+x}$ 479–481 - - in TmES 363, 368, 376 $- - in Tm_3Ga_5O_{12}$ 363 - - in TmPO₄ 363 - - in TmVO₄ 363 - of ⁵¹V - - in EuVO₄ 372 - - in HoVO₄ 372 - - in PrVO₄ 372 - - in TmVO₄ 372 numerical aperture of fibers 582, 584 (OH)⁻ 538, 539, 577 occupational preferences in ThMn12-type compounds 156, 157 one-center-expansion 634 optical confinement 581 optical fibers 580 orbit-lattice interaction in dielectric compounds 329, 337 see also electron-phonon interaction and electron-deformation interaction orbital 632 - contraction 614-622 - destabilization 614-622 - expansion 614-622 - stabilization 614-622 orbital ordering in dielectric compounds 330, 409, 428, 458 order parameter in dielectric compounds 332, 334, 422, 459 orthocobaltites, RCoO₃ 418 oscillator strength 542 - Ca₁₀(PO₄)F₂ (5FAP) 575

- Nd₂P₅O₁₄ (NdUP) 575 - Y3Al5O12 (YAG) 575 output coupling 564 overlap integral 314, 317, 322, 568 oxychlorides, ROCl 410-412, 420 oxyselenides, R2O2Se 410-412, 418 oxysulfates, R₂O₂SO₄ 410-412, 418 oxysulfides, R₂O₂S 410-412, 418 PDFFA (Pr³⁺-doped fluoride fiber amplifier) 590 paramagnetic shift in dielectric compounds 298, 348, 362, 369, 378 parastriction in dielectric compounds 354, 429-431, 433, 434 partition function 253 Pauli equation 614 Pauli Hamiltonian 637 Pauli spin matrices 631 Pauling model 683 РЬМоО₄ 573 Pekarian function 547, 548 perpendicular magnetic anisotropy (PMA) in R/T multilayers 119 - anisotropy analysis for Dy/M (M=Ta, Cu and Y) multilayers 125 - magnetic interactions 87, 88, 119, 121-124, 139 - model analysis for Dy/Co and Tb/Fe multilayers 124 - origin of 94, 99, 119-121, 125, 139, 140 - PMA analysis for Gd/T (T = Co, Fe) multilayers 125 – PMA model 121–124 structural anisotropy 99, 119, 125, 139 phase diagrams of dielectric compounds 460, 464 $- Dy_p Gd_{1-p} VO_4$ 467 - DyP_pV_{1-p}O₄ 469, 471 $- Dy_p Tb_{1-p} VO_4$ 466, 467 $- DyV_pP_{1-p}O_4 470$ $- Gd_p Dy_{1-p} VO_4$ 467, 470 $- \text{LiHo}_{p} Y_{1-p} F_{4}$ 469, 470 $- \text{LiTb}_p Y_{1-p} F_4$ 468 $- \text{Tb}_p \text{Dy}_{1-p} \text{VO}_4$ 467 $- \text{Tb}_p\text{Gd}_{1-p}\text{VO}_4$ 467 $- \text{Tb}_p \text{Yb}_{1-p} \text{VO}_4$ 467 $-(Tm_pY_{1-p})_2(SO_4)_3$ 469 Tm_pLu_{1-p}VO₄ 459, 466, 467 $-Tm_pTb_{1-p}VO_4$ 467 $-Y_p Dy_{1-p} VO_4$ 467 phosphate glass, KLi 573 phosphates, RPO₄ 304, 325, 339, 350, 419 photoemission spectra for NdCo10Cr2 258 - for YCo10V2 258

photon avalanche effect 561, 592 ASE emission at 850 nm 593 - anti-Stokes multiphonon sidebands absorption 563 - ESA and laser effects 564 - Er³⁺ in a ZBLAN fluoride glass 563 - LaCl₂:Pr³⁺ 593 – LiYF₄:Er³⁺ 563 - long rise times 562 - Nd³⁺ 561 - Ni²⁺ 561 - nonlinear dependences of transmission, emission, rise time 562 $- Pr^{3+} 562$ - Pr³⁺-doped LaCl₃ and LaBr₃ 561 - silica glass fibers 562 $- Sm^{3+} 561$ - Tm³⁺:YAlO₃ 562 - up-conversion spatial domains 564 - ZBLAN:Er³⁺ 593 photon echo 526 photon lifetime in a cavity 540 photon-trapping effects 550 - Cr³⁺ 550 - Yb³⁺ 550 2-photon up-conversion processes 557 photothermal experiments 578 piezomagnetic constants in dielectric compounds 336 piezospectroscopic data in dielectric compounds 338, 339 planar anisotropy in ThMn12-type compounds 216, 217, 236, 242, 266 polarized ion model 614 powder ASE (amplified spontaneous emission) - applications 540 --- holography 540 - - master oscillators for fusion lasers 540 - - transport of energy in fibers for medical applications 540 - spatial incoherence 539 - temporal coherence 539 Pr³⁺ - -doped fluoride fibers 592 - -doped systems 531 - electronic states 652 (Pr, Sm)Fe_{~6}Ga_{~6} 202 Pr-Co-Mn 156 Pr-Cu-Al 154 Pr-Fe-Ga 154 Pr--Mn--Ni 156 PrAlO₃ 306, 365 $PrBa_2Cu_3O_{6+x}$ 422 PrBr₃ 428

PrCl₃ 344, 428 PrCl₃·7H₂O 391 PrCo10Mo2 236 PrCo11 Ti 216 PrCr₄Al₈ 164 PrCu₄Al₈ 179 PrES (praseodymium ethylsulfate) 344, 428 PrF₃ 365, 386, 390, 706 PrFe₄Al₈ 170 $PrFe_xGa_{12-x}$ 204 PrFe5.5Ga6.5 206 $PrFe_{12-x}Mo_x$ 235 PrFe_{10.52}Re_{1.48} 242 Pr_{1.64}Fe_{7.2}Re_{4.8} 242 PrFe₁₀Si₂ 207, 208 $PrFe_{12-x}Ti_x = 211$ $PrFe_{11}TiC_{1-x}$ 262 $[Pr(H_2O)_n]^{3+}$ 702 $Pr^{3+}:LaCl_{3} = 562$ PrMn₄Al₈ 166 Pr(NO₃)₃.6H₂O 391 PrO 676 Pr(OH)₃ 344, 428 Pr₂(SO₄)₃·8H₂O 364, 391 PrTFMS (Pr trifluoromethane sulfonates) 344, 428 PrVO₄ 363, 366, 372, 391, 400 preferential occupation in ThMn12-type compounds 156, 157 primogenic repulsion 618 pseudopotential method 613 pseudopotentials 642-648 - comparison for Ce 655 pseudoquadrupole interaction in dielectric compounds 348, 369 pseudospin Bloch vector 519 - two-level system 517 pseudospin operators in dielectric compounds 340, 342, 360, 460 pumping sources for the Nd³⁺:YAG laser - iodine tungsten lamp 584 - laser diode 584 - rare gas arc lamp 584 pyrogermanates, R₂Ge₂O₇ 418 Q-switching 579 quadrupole interaction in dielectric compounds 310, 372 quantized electromagnetic field 515

quantum efficiencies 543

quantum wells 594

quantum yield 544

quantum electrodynamics 629, 634

quasi-laser-like emissions of powders 539 quasirelativistic methods 638-640 $(R, An)Cu_4Al_8$ 178 $(R, An)Cu_6Al_6$ 195 - magnetic investigations 195 Mössbauer experiments 195 $(R, An)Fe_xAl_{12-x}$ 195 $(R, An)Fe_4Al_8$ 169, 175 (R, An)Fe₅Al₇ 190 $(R, An)Fe_6Al_6$ 190 (R, An)Fe₅Al₇-type compounds 185 $(R, An)Fe_xAl_{12-x}$ systems 169–178, 197 (R, An)M₁₂ 157, 158 (R, An)M₄Al₈ 163 (R, An)M₆Al₆ 190 (R, An)Mn₄Al₈ 163 (R, An)T₄Al₈ 153 $(R, An)T_{12-x}M_x = 157$ $(R, An)T_xM_{12-x}$ -type compounds 162 (R, U)Mn₆Al₆ 190 R-Fe-Mo 156 $RBa_2Cu_3O_{6+x}$ 420, 479 - critical temperature 473, 476 - crystal electric field 479 - CuO chain fragments 473, 475, 485, 487 - Meissner fraction 473 mesoscopic phase separation 471 - mesoscopic structure 477, 478 - ordered phases 473, 475, 477-479 - oxygen diffusion 473, 475 -- coefficient 475, 489 - oxygen ordering 471, 475-477 - paramagnetic centers (copper-oxygen complexes, clusters) 488, 490 - room-temperature annealing 476 - structural transformations 473 - superconducting transition 472, 475 - superconducting volume fraction 472, 478, 481, 483, 490, 491 RBr₃ 410-412, 416 RCl₃ 410-412, 416 RCo10Si2 210 RCo10V2 229 RCr₄Al₈ 163 RCr₆Al₆ 190 RCu₄Al₈ 182 RCu₆Al₆ 195 R₂ dimers 680, 681 R-doped fibers for amplifiers and lasers 580 R-doped light-guiding active medium 599 R-doped planar waveguide amplifier and laser system 599 R-doped semiconductors 594, 597

oxygen impurities 598 RES (rare-earth ethylsulfate) 323 RF 677-680 RF₃ 304, 410–412, 415, 706 RF₈⁵⁻ 706 RFe₂ 160 R₂Fe₁₇ 270 R₈(Fe, Co)₇₆(V/Mo)₁₆ 264 $R(Fe, Co)_{12-x}Ti_x$ alloys 229 R(Fe, Co)₁₀V₂ 229 R(Fe, Me)₁₂C 263 RFe_xAl_{12-x} 198 RFe₄Al₈ 169, 175 magnetic susceptibility 175 RFe₅Al₇, Fe atom distribution 154 RFe₆Al₆, Fe atom distribution 154 RFe5Al7-type aluminides lattice parameters, magnetic properties 186 Mössbauer and neutron diffraction data 187 R₂Fe₁₄B 270 $RFe_{11-x}Co_xTi$ alloys 221 RFe₁₀Cr₂ 233, 248, 249 RFe_xGa_{12-x} 202 RFe₆Ga₆ 203 RFe10-11 Ga2-1 203 RFe_{~6}Ga_{~6}, energy products 202 $RFe_{12-x}M_x = 245, 270$ RFe10Mo2 155, 233, 234, 250 RFe10Re2 156 RFe₁₀Si₂ 155, 207, 247, 268 RFe₁₀SiC_x 262 RFe_{10.9}Ti_{1.1} 216 RFe11Ti 221, 247, 248, 251 R₈Fe₆₄Ti₈ 264 RFe₁₀Ti alloys 265 RFe_{10.9}Ti_{1.1} systems 222 RFe11Ti-type 220 $RFe_{11}TiC_{1-x}$ 262 RFe₁₀V₂ 222, 229, 230, 246–248, 252 $RFe_{12-x}V_x = 245$ RFe₁₀V₂ compounds 157 RHe³⁺ 682 **RKKY** interaction in metallic nanostructures 30, 48, 50, 69 - in ThMn₁₂-type compounds 182, 243 RMO₄ 304, 322 RMR (rejection mode ratio) in lasers 597 RM10Ti2 210 $RM_{12-x}V_x$ 222 RMn₄Al₈ - mixed-valent state 168 unit cell volume 168 RND (rare-earth nicotinate dihydride) 444 RO 660-676

R sublattice 249 RTFMS (R trifluoromethane sulfonates) 343, 409, 416 $RT_{12-x}M_x = 240$ RTi_{1.1}Fe_{10.9} 220 RTiFe10.25C0.25 261 RX₂ 685 RX3 685 RX₄ 685 RX" - atomization energy 687 - geometry 686, 687 - ionization potential 686 RZn₂ 160 161 RZn₁₂ Rabi frequency 522 radiative damping constant 526 radiative lifetime 520 $-T_1$ 524 random magnetic anisotropy (RMA) in metallic nanostructures 36, 37, 70 rapid quenching of ThMn₁₂-type compounds 264, 265 rare-earth cuprates 323, 325 see also RBa2Cu3O6+x rare-earth (R) ion systems 531 rare gas compounds (RHe³⁺) 682 Rb₂NaHoF₆ 305 Rb₂NaRF₆ 305, 306 Rb₂NaTbF₆ 364 R(cp)₃ 690 relativistic effects 609, 614, 616, 617, 619, 627 - Au, Hg, Eka-Au, Eka-Hg 626 - binding energy 620 - bond energies 621 - bond energy changes 622 - bond lengths 619, 620 - direct 615 - excitation energies 618 - indirect 615 - interpretation 619 - ionization potentials 618 - orbital energies 616 $-\langle r \rangle$ expectation values 616 - spatial origin 617 relativistic many-electron Hamiltonians 629 relaxation time, see Bloch longitudinal and Bloch transverse relaxation times resonant radiative transfer 550 R@C_n 695-700 Russell-Saunders 257 SF theory, see spin fluctuation theory

SG, see spin glass

SHG (second-harmonic generation) 557 SRT (spin-reorientation transition) in ThMn12-type compounds 175, 176, 220, 221, 229, 240, 243, 247-252 - influence of pressure 252 - temperature 175, 207, 230, 231, 246, 251, 276 ScFe₆Ga₆ 203 ScFe₆Ga₆-type structure 202 scalar crystal field parameter 571 Schrödinger equation 615, 629 Sc@C₈₂ 700 self-consistent field 330, 331, 460, 462, 633 self-consistent spin-polarized calculations 254, 255, 258 self-doubling visible lasers 580 self-focusing effect 580 self-quenching 564, 565, 567, 568, 570, 571 - linear behavior with N 569 - quadratic dependence on N 569 - rate R_0 of Nd³⁺ (⁴F_{3/2}) and Tb³⁺ (⁵D₃) $- - LnP_5O_{14} = 570$ $- - NaLn(WO_4)_2 570$ resonance condition 572 Sellmeier formula 578 semiconducting 1II-V compounds doped with R 594 semirelativistic approximation 254 sesquioxides, R2O3 420 shell structure effects 627 - Au, Hg, Eka-Au, Eka-Hg 626 short-range order in ThMn12-type compounds 188 - ferrimagnetic 188 - magnetic 255 silica and fluoride fibers 584 silicate flint glass 573 silicon-based optoelectronic devices 599 single-crystal metallic nanostructures 1-76 single crystals of ThMn₁₂-type compounds 169, 175, 176, 178, 207, 243, 248, 249 single-mode semiconductor lasers by coupling to R-doped insulators 594 singlet magnetism 409 Slater determinant 632 slope efficiency of lasers 564 Sm-Co-Mn 156 Sm-Cu-Ga 154 Sm-(Fe, Co)-V 265 Sm-Fe-Al 154 Sm-Fe-Ga 154 Sm-Fe-T systems 265 Sm-Fe-Ti alloys 264-266 Sm-Fe-Ti derivatives 263 - ribbons, magnetic properties 264

Sm--Fe--V 265 Sm--Mn--Ni 156 SmCo₁₀Mo₂ 236, 237 SmCo11Ti 216 $SmCo_{12-x}V_x = 227$ SmCr₄Al₈ 163, 164 SmCu₄Al₈ 179 SmFe₁₂ 160, 161 Sm(Fe, Al)₁₂C 263 Sm(Fe, Co)11 Ti 265 Sm(Fe, Cu)₁₂C 263 Sm(Fe, Ga)12C 263 SmFe₂, hysteresis loop 160 Sm(Fe, T)12 265 Sm(Fe, V)12C 263 SmFe₄Al₈ 170 SmFe5Al7 185-187 SmFe₈Co₂Mo₂ 237 SmFe_{10-x}Co_xSi₂ 210, 247 SmFe₈Co₃Ti 247 $SmFe_{10.8-x}Co_{x}Ti_{1.2}$ 247 $SmFe_{11-y}Co_yTi_x = 217$ $Sm(Fe_{11-x}Co_x)Ti$ 221 SmFe_{11-x}Co_xTi 246 Sm10Fe50Co30Ti10 266 Sm₁₀Fe₇₀Co₁₀Ti₁₀ 266 SmFe_{8.5}Co₂V_{1.5} 227 SmFe₉₅CoV₁₅ 227 SmFe₁₀Cr₂ 232 SmFe_xGa_{12-x} 204 Sm₈Fe₇₅Ga₂Ti₈V₈ 264 Sm₈Fe_{75.5}Ga_{0.5}Ti₈V₈ 264 Sm8Fe76GaTi8V8 264 $SmFe_{12-x}Mo_x = 235$ Sm₈Fe₈₀Mo₁₂ 265 Sm₈Fe₈₂Mo₁₀ 266 (Sm₁₂Fe₇₈Mo₁₀) 266 Sm10 Fe80 Mo5 Ti5 266 $SmFe_{12-x}Re_2$ 242 Sm1.2Fe7.5Re4.5 242 SmFe₁₀Si₂ 157, 208 Sm_xFe_yTi_z 265 SmFe₁₀Ti 245 SmFe11Ti 157, 248 SmFe_{11.75}Ti_{1.04} 265 $SmFe_{12-x}Ti_x = 211, 212$ Sm₈Fe₈₃Ti₉ 264 Sm₁₉Fe₇₃Ti₈ 266 Sm₂₀Fe₇₀Ti₁₀ 266 Sm₂₆Fe₆₄Ti₁₀ 266 SmFe11 Ti-alloy 265 $SmFe_{10.8}Ti_{1.2}B_x = 263$ Sm₁₀Fe₈₀Ti_{7.5}B_{2.5} 265 Sm₈Fe₇₆Ti₇CrV₈ 264

Sm₈Fe₇₆Ti₇MoV₈ 264 Sm8Fe76Ti7NbV8 264 Sm₈Fe₇₆Ti₈V₈ 264 Sm₈Fe₇₆Ti₇WV₈ 264 Sm₈Fe₇₆Ti₆Zr₂V₈ 264 Sm₈Fe₇₆Ti₇ZrV₈ 264 $SmFe_{11}TiC_{1-x}$ 262 SmFe₁₀TiCr 232 SmFe10TiMn 233 SmFe₁₀TiV 224 Sm_{0.89}Fe₁₀V₂ 264 Sm_{0.95}Fe₁₀V₂ 264 $SmFe_{12-x}V_x$ 224 Sm₁₂Fe₇₃V₁₅ 266 Sm15Fe70V15 266 $SmFe_{12-x}W_x$ 241 $(SmH(cp)_2)_n = 689$ SmMn₄Al₈ 166 Sm pseudoternaries in ThMn12-type compounds 210 Sm10Si2 209 SmTi_{1.1}Fe_{10.9} 220 SmZn₁₂ 161 - electric resistivity 162 $Sm(cp)_{2}^{q+}$ 689 sol-gel method 577 space groups of the lanthanide compounds 410-412 sparkle model 651, 704 specific heat - of dielectric compounds 422, 469 - of lasers 578 - ThMn₁₂-type compounds 183 spectroscopic quality parameter 575, 577 spherical operators 308, 316 spherical polynomials 307, 315, 316 see also Stevens operators spin echo 377, 405, 441, 444, 448, 486 - decay 448, 486 - shape 442, 448 spin fluctuation (SF) theory 257, 258 spin glass in dielectric compounds 469–471 in ThMn₁₂-type compounds 176, 178, 185, 188, 199, 200 spin Hamiltonian 340, 387, 389, 414, 426, 430, 479 - nuclear 348, 363, 369 - parameters 344, 390, 391, 480 spin-lattice relaxation 379, 383-386, 392-396, 405, 453, 455, 456, 471, 484, 487 - of Ce^{3+} in LiTmF₄ 393 - of Er³⁺ in TmES 393

- of ¹⁹F in LiTmF₄ 385 - of Nd3+ - - in LiTmF₄ 393 -- in TmES 393 - of ¹⁴¹Pr in Pr₂(SO₄)₃.8H₂O 382 - of protons in TbES and DyES 454 - of Tb³⁺ in TmES 393 - of ¹⁶⁹Tm -- in LiTmF₄ 382, 385 $- - in TmBa_2Cu_3O_{6+x}$ 484, 489 - - in TmES 382, 383, 400 - - in TmPO₄ 382 - - in TmVO₄ 382 - of Yb³⁺ in LiTmF₄ 393 spin-polarized band calculations in ThMn12-type compounds 254, 257, 258 see also band-structure calculations spin-polarized DOS (density of states), see DOS spin-reorientation transition, see SRT spin slip in metallic nanostructures 13, 25 spin structure in ThMn₁₂-type compounds 188 spin-orbit coupling 257, 647 spin-orbit effects 613 spin-phonon interaction 341, 381 - for Dy:LiRF₄ 433 - for Er:LiRF₄ 433 spin-rotational interaction 341 spin-spin relaxation 378, 405, 453, 456 spinor 632 spontaneous emission 519, 522, 534 - amplified by stimulated emission, see ASE - damping 523 - damping of the Rabi oscillation 522 - probability 521 spontaneous lifetime 526 Stark spectrum 317 Stark splitting 571, 572 Stevens factors 243 Stevens operators 223, 307 – equivalents 249 stoichiometric laser 599 - materials 567 minilaser 567 Stokes' law 590 stress tensor 311 strong- and weak-quenching materials 568 strong exchange limit in ThMn12-type compounds 244 strong hysteresis effects in ThMn12-type compounds 202 sublattice anisotropy in ThMn₁₂-type compounds 225 sublattice displacements in dielectric compounds 309, 327, 335, 356, 357

substrate for metallic nanostructures 17 sulfates, hydrated 409 superconducting volume fraction 487 superconfiguration model 627-629 superfluorescence 512, 523, 527 - applications 536 - - coherent sources for X-rays and γ-rays 536 - - noise figure below the spontaneous emission noise limit 536 – triggering spectroscopy 536 - Arecchi-Courtens cooperation time 530 - conditions for SF 530 - critical cooperation distance 530 - delay 529 - escape time 530 - initial tipping angle 529 - KBr:O₂⁻ 532 $- \text{KCl:O}_2^-$ 532 - KI:0,-532 - large-absorption condition 530 – LiYF₄:1%Er³⁺ 533 - LiYF₄:Er³⁺ 534, 535 $-\frac{1}{2}\pi$ pulse 527 $-\pi$ pulse 527 - R-doped system 533 - R ions 531 - self-organization 529 - self-organized superradiance 527 - threshold length 530 superfluorescent lifetime 528 superhyperfine interaction 307, 311, 443 superlattice 4, 6 see also Dy/Lu, Dy/YDy, Dy/Y, Dy/Zr, Er/Y, Gd/Dy, Gd/Y, Ho/Er, Ho/Lu, Ho/Y, and Nd/Y - epitaxial 3, 16, 39 - metallic R-R nanostructures 39-71 superposition model 338 superradiance 512, 523, 525 - active superradiance 525 - limited superradiance 525 - macro dipole 525 - microcavity 528 - passive superradiance 525 - R ions 531 - reaction field 525 - strong superradiance 525 - YAG:Nd 533 superradiant lifetime 526 susceptibility - conduction electron 8, 9 - diamagnetic 481, 491 - dielectric 426-428 - dynamic 405

susceptibility (cont'd) - magnetic 168, 336, 346, 358-362, 371, 378, 402, 416, 422-424, 444, 469 - multipolar 353 - non-local 8 - single-ion 333, 426 - third-order 359 TFMS, see trifluoromethane sulfonates (Tb, U)Fe₁₀Si₂ 286 Tb-Fe-Ga 154 TbAsO₄ 305, 319, 322, 345, 415, 417, 419, 458 Tb(BrO₃)₃.9H₂O 415 TbCo10Mo2 236 Tb1.03Co10Mo1.94 236 TbCo11Ti 216 $TbCo_{12-x}V_x = 227$ TbCr₄Al₈ 164 TbCu7-type phase 265 TbCu₄Al₈ 179 TbCu₆Al₆ 196 TbES (terbium ethylsulfate) 299, 319, 323, 344, 405, 407, 415, 417, 439-442, 448, 449, 452 TbF₃ 305, 415, 424 TbF₈⁵⁻ 706 TbFe_{10.8-x} 252 TbFe_xAl_{12-x} 198, 199 TbFe₄Al₈ 171 TbFe₅Al₇ 186-188 - neutron diffraction 186, 188 TbFe₆Al₆ 192 $TbFe_{10.8-x}Co_xW_{1.2}$ 240, 252 $TbFe_{10.8-x}Co_xW_{1.2}$ 241 $TbFe_{10.8-x}Co_{x}W_{2}$ 240 TbFe₁₀Cr₂ 232, 250, 251 $TbFe_xGa_{12-x}$ 204 TbFe10Mo2 250 $TbFe_{12-x}Mo_x$ 236 $TbFe_{12-x}Re_2$ 242 TbFe10Si2 208 TbFe₁₁Ti 248, 250 $TbFe_{12-x}Ti_x$ 213 $TbFe_{11}TiC_{1-x}$ 262 TbFe105V15 248 $TbFe_{12-x}V_x = 225$ Tb₃Ga₅O₁₂ 415 TbMn₁₂ 158, 160 TbMn₄Al₈ 167 TbMn₆Al₆ 191 TbOCl 420 Tb(OH)₃ 344, 415, 417 Tb2O2SO4 345, 415 TbPO₄ 305, 319, 322, 419 Tb₂(SO₄)₃·8H₂O 414

TbTFMS (Tb trifluoromethane sulfonate) 415 Tb₂Ti₂O₇ 434 $Tb_{1-x}U_xFe_{10}Si_2$ 275, 276 ТЬОО4 305, 319, 322, 345, 415, 417, 419, 429, 458, 466 TbZn₁₂ 161 electric resistivity 162 tellurite glass 573 ternary actinide AnM5Al7 aluminides - lattice parameters, magnetic properties 189 ternary AnFe₄Al₈-type aluminides, lattice parameters, magnetic properties 177 ternary carbides and carbosilicides of various types, composition, lattice parameters, magnetic properties 262 ternary miscellaneous compounds with Ti, composition, lattice parameters, magnetic properties 219 ternary (R, An)Cr₄Al₈-type aluminides - lattice parameters, magnetic properties 164 ternary (R,An)Cu₄Al₈-type aluminides, lattice parameters, magnetic propeties 179 ternary (R, An)Fe₆Al₆-type aluminides, lattice parameters, magnetic properties 192 ternary (R, An)M₆Al₆-type aluminides, lattice parameters, magnetic properties 191 ternary (R, An)Mn₄Al₈-type aluminides, lattice parameters, magnetic properties 166 ternary $RCo_{12-x}Mo_x$ compounds, composition, lattice parameters, magnetic properties 236, 237 ternary RCo11 Ti-type compounds, lattice parameters, magnetic properties 216 ternary RCo_{12-r}V_r compounds, composition, lattice parameters, magnetic properties 227 ternary RCu₆Al₆-type aluminides, lattice parameters, magnetic properties 196 ternary R(Fe, Co)_{12-x}V_x-type compounds, composition, lattice parameters, magnetic properties 223 ternary RFe4Al8-type aluminides, lattice parameters, magnetic properties 170 ternary RFe_{11 - v}Co_vTi_x-type compounds, composition, lattice parameters, magnetic properties 217 ternary RFe₁₀Cr₂-type compounds, lattice parameters, magnetic properties 232 ternary RFe_xGa_{12-x}-type gallides, composition, structure type, magnetic properties 204 ternary RFe_{12-x}Mn_x-type compounds, composition, lattice parameters, magnetic properties 233

ternary RFe_{12-r}Mo_r-type compounds, composition, lattice parameters, magnetic properties 235, 236 ternary $RFe_{12-x}Ti_x$ -type compounds, composition, lattice parameter, magnetic properties 211 ternary $RFe_{12-x}W_x$ -type compounds, compositions, lattice parameters, magnetic properties 241 ternary RM10Si2-type silicides, lattice parameters, magnetic properties 208 ternary RRh₆Al₆-type aluminide, magnetic properties 197 tetrafluorides, LiRF₄ 302, 323-325, 338, 339, 350, 419, 433 $Th(C_8H_8)_2$, see thorocene ThCr₄Al₈ 165 ThCr₂Si₂ 168 ThCr₂Si₂-type compounds 163 ThCu₄Al₈ 180, 182 ThFe4Al8 176-178 ThMn₁₂-type compounds - lattice parameters 154-156, 160, 161, 164-167, 170-174, 177, 179-181, 186, 189, 192-194, 196, 204, 205, 208, 209, 211-214, 216-218, 220-227, 231-233, 235-242, 262, 263, 268, 269, 274, 276, 277, 280, 283 - magnetic properties 157-286 - spin-reorientation transition 247-252 - structure, description 151-157 ThMn₄Al₈ 167, 168 ThO 670 - population analysis 670 ThO₂ 684 thermal conductivity of laser materials 577 thermal expansion of laser materials 577, 578 thermal hysteresis in SmFe₅Al₇ 188 thermal properties of laser materials 577 thermal stability of the wavelength 597 thermal variation of optical path in laser materials 577 thermoelectric power in CeCu₄Al₈ 178 thermolensing process in laser materials 577 thermomagnetic effect in DyFe₄Al₈ 176 thin films - of ThMn₁₂-type compounds 160, 207 $- - SmFe_{12} = 160$ - of the metals 14-39 thorocene (Th(C₈H₈)₂) 689, 690 tight-binding calculations for ThMn12-type compounds 255 time-dependent effects in SmFe₅Al₇ 188 Tm₃Al₅O₁₂ 391 TmAsO₄ 319, 322, 364, 392, 429, 458 TmBa₂Cu₃O_{6+x} 318, 323, 325, 491

- broadening of Tm NMR line -- homogeneous 484 ----- inhomogeneous 482, 483, 487 - crystal electric field 479 - non-exponential ¹⁶⁹Tm relaxation 487, 488 - oxygen ordering 482, 488 - paramagnetic centers (copper-oxygen complexes, clusters) 487-489 - room-temperature annealing 489 TmBa2Cu3O6.5 318 TmBa₂Cu₄O₈ 318 TmCo10Mo2 237 Tm_{1.03}Co₁₀Mo_{1.94} 237 TmCr₄Al₈ 164 TmCu₄Al₈ 180 TmCu₆Al₆ 196 Tm3+-doped – fiber 592 - halide crystals 561 Tm³⁺ fluoride fiber laser 592 TmES (thulium ethylsulfate) 299, 318, 323, 349, 362, 364, 370, 376, 390, 392, 393 TmFe₄Al₈ 173 TmFe5Al7 186, 187 TmFe₆Al₆ 194 TmFe₁₀Cr₂ 232 TmFe_xGa_{12-x} 205 TmFe_{12-x}Mo_x 236 $TmFe_{12-x}Re_2$ 242 TmFe10Si2 209 $TmFe_{12-x}Ti_x = 214$ $TmFe_{11}TiC_{1-x}$ 262 $TmFe_{12-x}V_x$ 226 Tm₃Ga₅O₁₂ 390 $[Tm(H_2O)_n]^{3+}$ 702 TmMn₄Al₈ 167 TmMn₆Al₆ 191 TmO 676 TmPO₄ 305, 318, 322, 350, 353–356, 359, 361, 364, 392, 400 - magnetization 360 TmVO₄ 305, 319, 322, 364, 392, 400, 429, 458, 461, 466 TmZn₁₂ 161 transferred hyperfine interaction in dielectric compounds 373, 443 see also superhyperfine interaction transverse relaxation - mechanisms 379-386 - of ¹H in TbES and DyES 452 - of ¹⁶⁹Tm $- - in TmBa_2Cu_3O_{6+x}$ 484, 486 - - in TmES 384 - rate T_2^{-1} 379–386, 456

SUBJECT INDEX

tribromides, RBr₃ 410-412, 416 trichlorides, RCl₃ 410-412, 416 trifluorides, RF₃ 304, 410-412, 415 trifluoromethane sulfonates, R(CF₃SO₃)₃:9H₂O (RTFMS) 343, 409, 416 tris(dipivaloylmethanato)(2,2':6',2"terpyridine)europium(III) 705 turn angle in metallic nanostructures 10, 12, 30, 31,48 lock-in state 13, 25, 31, 57 two-level atom - nutation frequency 516 - photon-echo 519 $-\frac{1}{2}\pi$ pulse 519 $-\pi$ pulse 519 - pseudo-spin Bloch vector 519 - Rabi equation in the quantized approach 516 - Rabi frequency 516 - synchronous exchange between field and atom 516 U-Ni-Si 272 $U(C_8H_8)_2$, see uranocene UCo10Si2 157, 246, 268, 270-272 UCr₄Al₈ 163, 165 UCu₄Al₈ 180, 182 UCu_{4+x}Al_{8-x} 154, 183, 185, 195, 286 - heavy-fermion like behavior 183 UFe_xAl_{12-x} 200, 201 UFe₄Al₈ 169, 176-178, 286 $UFe_{4+x}Al_{8-x}$ 154 UFe₅Al₇ 188, 202 UFe₆Al₆ 194, 195 UFe₈Al₂Si₂ 284 UFe₁₀ Al_rSi₂ 283–285 $UFe_{10-x}(Co, Ni)_xSi_2$ 279 UFe6Co3AlSi2 279 UFe_{10-x}Co_xSi₂ 277, 278, 281 UFe_xCu_{4-x}Al₈ 184, 185 UFe10Ge2 273 UFe10M2 273 UFe10Mo2 155, 268, 272, 273 $UFe_{10-x}(Ni, Co)_xSi_2 = 281$ UFe6Ni4Si2 247 UFe₈Ni₂Si₂ 247 $UFe_{10-x}Ni_xSi_2$ 279, 280 UFe10Re2 156, 268, 273 UFe₁₀Si₂ 155, 157, 246, 267–273, 284, 286 UFe_{12-r}Si_r 156, 267, 269 UFe10Si1.75Mo0.25 273 UM10M' compounds 273 - lattice parameters, magnetic data 268 UMn_xAl_{12-x} 168 UMn₃Al₉ 168

UMn₄Al₈ 167, 168 $UMn_{4+xA}Al_{8-x}$ 154 $UMn_{4+x}Al_{8-x}$ 195 UMn₆Al₆ 191 $UMn_{4+x}Al_{8-x}$, range of homogeneity 183 UNi_{9.5}Co_{0.5}Si₂ 281, 282 UNi_{10-x}Co_xSi₂ 281 UNi₈Cu₂Si₂ 282 UNi₉CuSi₂ 283 UNi₂Si₂ 272 UNi10Si2 157, 185, 268, 271, 272, 281-283 UT₁₀Si₂ 270 $U_{1-x}Y_{x}Fe_{10}Si_{2}$ 274, 275 U@C28 696, 697 U@C60 697 $U@C_{60}^{+}$ 697 up-conversion 549, 555, 558 2-photon up-conversion comparison 557 - APTE (Addition de Photon par Transferts d'Energie) effect 556 - cooperative effects 556 - distinction between APTE and cooperative effects 560 - line-narrowing effect 559 *n*-photon 557 up-conversion lasers 590-592 diode-pumped 591 uranium ThMn₁₂-type compounds 154 uranocene $(U(C_8H_8)_2)$ 689 valence-electron method 641 valence of cerium ThMn₁₂-type compounds 152 Van Vleck paramagnets 298, 318, 346-402 - EPR of impurity lanthanide ions 388, 390 $- - Ce^{3+}$ 390 $- - Dy^{3+}$ 390 $- - Er^{3+}$ 390 - - Gd³⁺ 391 $- - Nd^{3+}$ 390 $- - Yb^{3+}$ 390 - magnetostriction in 354 - NMR in 363, 372 see also nuclear magnetic resonance Van Vleck susceptibility 341, 347, 362, 372 vanadates, RVO₄ 304, 325, 339, 419, 460 vapor-deposited Er³⁺-doped glass waveguide 599 variational collapse 633, 635 Vegard's law for ThMn₁₂-type compounds 233, 238, 267, 275, 279 vibronic reduction in dielectric compounds 330, 343 vibronics 544, 546 volume density of cavity modes 541

wave functions of Ln^{3+} ions in crystal fields 320 wave vector, see turn angle wavelength division multiplexing (WDM) 588 weak CEF 182 weak ferromagnetism 176 Weisskopf-Wigner damping 519 Wood-Boring Hamiltonian 638-640 XANES (X-ray absorption near edge structure) of ThMn₁₂-type compounds 175 XPS-3d core level spectroscopy of ThMn12-type compounds 175 XY model of dielectric compounds 346, 417, 428 Y-Co-Mo 156 Y-Fe-Cr 156 Y-Fe-Ga 154 Y-Fe-Mo 156 Y-Fe-Ti 156 Y-Fe-V 156 YAG $(Y_3Al_5O_{12})$ 569, 572, 576 YAG:Er³⁺ 585 YAG:Nd 567 YALO (YAlO₃) 576 YAlO₃(La, Nd) 573 Y₃Al₅O₁₂(La, Nd) 573 YBa₂Cu₃O_{6+x} 478, 483, 490 YBa₂Cu₄O₈ 475 YCo10Cr2 232 YCo10Mo2 236, 237 YCo10.5Mo1.5 246 Y_{1.03}Co₁₀Mo_{1.94} 236 YCo10Si2 209, 258, 272 YCo11Ti 216, 244 YCo₁₀V₂ 255, 258 $YCo_{12-x}V_x$ 227 YCr_4Al_8 164 YCu₄Al₈ 179 YES (yttrium ethylsulfate) 302 YFe₁₂ 161, 256, 259 $Y(Fe, Co)_{12-x}T_x$ 259 Y(Fe, V)12 259 $Y(Fe_{1-v}Co_{v})_{12-x}Mo_{x}$ 237 $Y(Fe_{1-x}Co_x)_{10,8}Re_{1,2}$ 242 $Y(Fe_{1-x}Co_x)_{10}Si_2 = 210$ $Y(Fe_{1-x}Co_x)_{10.8}W_{1.2}$ 241 $Y(Fe_{1-x}Ni_x)_{11}Ti = 219$ $Y(Fe_{1-x}Si_x)_{11}Ti = 219$ YFe_xAl_{12-x} 200, 201 YFe₄Al₈ I69, 170, 175, 176, 200 YFe5Al7 186, 187 YFe₆Al₆ 192, 200 $YFe_{10.5-x}Co_xMo_{1.5}$ 238, 252

WO₄Ca 573

- magnetic phase diagram 239, 252 $YFe_{10-x}Co_xSi_2$ 210, 278 $YFe_{10.8-x}Co_{x}Ti_{1.2}$ 247 $YFe_{11-\nu}Co_{\nu}Ti_{x}$ 217 $YFe_{10-x}Co_xV_2$ 231, 246 YFe₁₀Cr₂ 232, 233, 254–256 YFe_xGa_{12-x} 204, 206 YFe_{12-x}Ga_x system 203 $YFe_{12-x}M_x = 256$ $YFe_{12-x}Mn_x$ 233 YFe8M04 258 YFe9M03 258 YFe10Mo2 273 YFe10.5 Mo1.5 246 YFe₁₁Mo 258 $YFe_{12-x}Mo_x$ 235, 258, 259 $YFe_{11-r}Ni_rTi 222$ YFe₁₀Re₂ 246, 273 YFe_{10.8}Re_{1.2} 273 YFe_{12-x}Re₂ 242 YFe₁₀Si₂ 207, 208, 244, 269-271, 275 $YFe_{12-x}Si_x$ 269 $YFe_{11-x}Si_xTi$ -type 222 YFe108Ti12 246 YFe11 Ti 257, 258 $YFe_{12-x}Ti_x$ 211, 257 $YFe_{11}TiC_{1-x}$ 262 YFe₁₁TiN 257 $Y_{1-b-c}Fe_bV_c$ 259 YFe₁₀V₂ 244, 246, 254–256 YFe_{12-x}V_x 223, 229, 244, 245, 257 $YFe_{12-x}W_x = 241$ YMn₁₂ 158-160 YMn₄Al₈ 166, 168 YMn₆Al₆ 190, 191 YMn_{12-x}Fe_x-type 233 YNi₁₀Si₂ 157, 272 YPO₄ 305, 350 YScO₃ 576 Y₀₅U₀₅Ni₁₀Si₂ 272 YVO₄ 305, 573 YZn₁₂ 161 Yb₂ 681 Yb³⁺, in InP 598 Ybⁿ⁺, electronic states 653, 654 Yb-Co-Ga system 206 Yb-Cu-Al 154 Yb³⁺-Er³⁺ system 591 Yb-Fe-Ga 154 Yb³⁺-Ho³⁺ system 591 YbBa₂Cu₃O₇ 318, 323 YbCr₄Al₈ 163, 164 YbCu₄Al₈ 180, 182 - XPS 182

YbCu₆Al₆ 195, 196 YbF 677 - electronic states 679 - population analysis 680 - spectroscopic constants 679 - spin density 680 YbF₃ 706 YbF₆³⁻ 706 YbF⁵⁻₈ 706 YbFe₄Al₈ 173 YbFe5Al7 186, 187 YbFe₆Al₆ 190, 194, 195 - Mössbauer experiments 195 $YbFe_xGa_{12-x}$ 205 YbH 657 - electronic states 659 - population analysis 659 - spectroscopic constants 659 - spin density 659 YbH₂ 684

Yb Mn_4Al_8 167 Yb Mn_6Al_6 191 YbO 672 - electronic states 674–676 - population analysis 673, 675 - spectroscopic constants 674, 675 Yb VO_4 419 Yb Zn_{12} 161 Y@ C_{82} 700 Young's modulus 351, 361 ZBLAN (Zr, Ba, La, Al, Na fluoride) glass fiber

– amplifier 589

- doped with Er³⁺ 588
- doped with Pr^{3+} 590
- doped with Tm³⁺ 590
- Zeeman energy in dielectric compounds 310, 321, 342
- Zeeman Hamiltonian in dielectric compounds 348, 388, 450
- ZrF₄-BaF₂-LaF₃-AlF₃-NaF (ZBLAN) glass 585