

HANDBOOK ON THE PHYSICS AND CHEMISTRY OF RARE EARTHS VOLUME 42

HANDBOOK ON THE PHYSICS AND CHEMISTRY OF RARE EARTHS

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HANDBOOK ON THE PHYSICS AND CHEMISTRY OF RARE EARTHS

VOLUME 42

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Jean-Claude G. Bünzli and Vitalij K. Pecharsky

These elements perplex us in our reaches [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)

Volume 42 of the Handbook on the Physics and Chemistry of Rare Earths adds two chapters to the series which are devoted to the description of fundamental thermodynamic and electronic properties of simple compounds versus temperature or pressure. Chapter 252 deals with structural and thermal properties of rare-earth compounds under high pressure in connection with their electronic and magnetic properties. The latter properties in condensed matter are dominated by electron correlations: for instance, high- T_c superconductivity is thought to originate from strong fand d-electron correlations. High pressure is an ideal tool to investigate these phenomena since the physical properties of materials on the border of magnetic instability depend on this parameter. The chapter entails five sections devoted to structural properties, thermal properties, new electronic phase transitions, and other phenomena such as pressure-induced magnetic order or negative magnetoresistance. Chapter 253 presents a systematic and critical evaluation of thermodynamic parameters for rareearth fluorides and chlorides in both gaseous and solid (or liquid) phases. A total of 105 individual compounds are scrutinized and methods are proposed to determine their thermodynamic functions over a wide temperature range (0–3000 K). Dependences of Gibbs free energy with respect to temperature are presented in an analytical form and the corresponding polynomials are cataloged in the appendix. These data together with the listing of formation, sublimation, and atomization enthalpies represent an impressive set of parameters which allows one to recalculate missing (or questionable) experimental data and to evaluate stability constants. Each chapter finishes with a perspective of new trends in the research field.

CHAPTER 252. THERMAL AND ELECTRONIC PROPERTIES OF RARE-EARTH COMPOUNDS AT HIGH PRESSURE

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Pressure is an excellent tool that makes possible many types of phase transitions in condensed matter, including quantum phase transitions. The present status of research on rare-earth compounds exhibiting borderline electronic and magnetic states is reviewed in this chapter. The authors demonstrate that effects of pressure on the physical properties of rare-earth compounds are mainly dominated by competition between the Kondo effect and Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions, which are functions of Kondo coupling. On the basis of this consideration, a general phase diagram (also called Doniach phase diagram) can be constructed as a function of Kondo coupling or of pressure. The diagram is used throughout the chapter to explain the behavior of materials. The chapter begins with the presentation of structural and elastic properties, followed by a discussion of thermal properties of selected compounds under pressure. Novel electronic phases and pressure-induced crossovers are then discussed. The chapter ends with the description of materials that are expected to show unforeseen pressure-induced electronic states.

CHAPTER 253. THERMODYNAMIC PROPERTIES OF LANTHANIDE FLUORIDES AND CHLORIDES IN THE GASEOUS AND CONDENSED STATES

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The chapter is devoted to the development of methods for calculating the thermodynamic properties of molecular gaseous and solid (or liquid) lanthanide fluorides and chlorides $R_m X_n$ (R = La–Lu; X = F, Cl; m = 1, n = 1-3; m = 2, n = 6) in a wide temperature range (0–3000 K).

Methods for the systematic calculation of thermodynamic functions as well as for estimating experimental data that are lacking are obtained on the basis of correlations between the electronic structure of lanthanide ions and the properties of these substances on molecular and macroscopic scales. The level of accuracy so attained is quite satisfactory. The methodology presented in the chapter and associated tabulated data have fundamental importance, as they facilitate the description of thermodynamic properties of related compounds not yet studied or for which experimental data are unsatisfactory.

The highlight of the chapter is the presentation in an analytical form of the temperature dependences of the reduced Gibbs free energy for 105 individual compounds, supplemented by the listing of their formation enthalpy under standard conditions $\Delta_f H^{\circ}(0)$, as well as of the atomization enthalpies $\Delta_{at} H^{\circ}(0)$ for the gaseous compounds and the sublimation enthalpies $\Delta_{sub} H^{\circ}(0)$ for solid-state samples. These extensive data represent complete and consistent sets and may therefore be incorporated into relevant databases or individual programs for routine calculations of the thermodynamic parameters for equilibria involving the participation of rare-earth fluorides or chlorides.

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CHAPTER **252**

Thermal and Electronic Properties of Rare Earth Compounds at High Pressure

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Abbreviations				
α	thermal expansion coefficient			
α_{mag}	the magnetic contribution to α			
γ	electronic specific heat coefficient			
ε _F	Fermi energy			
κ	the compressibility			
κ_i	linear compressibilities along <i>i</i> -axis ($i = a, b, \text{ or } c$)			
ρ	resistivity			
τ	wave vector			
ω_{s}	angular frequency			
<i>∆</i> (0)	superconducting gap at $T = 0$			
Γ	Grüneisen parameter			
$\Delta l/l$	linear thermal expansion			
Δ_{mag}	energy gap of antiferromagnetic magnon			
Θ_{D}	Debye temperature			
A^{-}	coefficient of T^2 term in resistivity			
AFM	antiferromagnetism			
B_0	bulk modulus			
B_0'	pressure derivative of bulk modulus			
BCS	Bardeen–Cooper–Schrieffer			
$B_{\rm T}$	the isothermal bulk modulus			
С	heat capacity			
$C_{\rm ac}$	alternating current specific heat			
CEF	crystalline electric field			
СК	concentrated Kondo			
$C_{\rm s}$	heat capacity of superconductivity			
C_V	the specific heat at constant volume			
D(E)	density of state at energy <i>E</i>			
Ε	energy			
FRP	fiber-reinforced plastic			
FWHM	full width at half maximum			
g_0	the degeneracy factor of ground state			
<i>g</i> ₁	the degeneracy factor of exited sate			
Η	magnetic field			
ħ	reduced Planck constant or Dirac constant			
HF	heavy fermion			
hpp	high-pressure phase			
HRC	Rockwell hardness in C-scale			
IC	incommensurate			

k _в lpp	Boltzmann constant low-pressure phase
MPMS	magnetic property measurement system
n	electronic density
ND	neutron diffraction
NMR	nuclear magnetic resonance
P	pressure
P_{c}	critical pressure
Q	wave vector
q_1	propagation vector
R	gas constant
SC	superconductivity
Т	temperature
T_0	a characteristic temperature
$T_{\rm C}$	Curie temperature
T_{c}	superconducting transition temperature
$T_{\rm F}$	the temperature where electron becomes in Fermi liquid
	state
$T_{\mathbf{K}}$	Kondo temperature
$T_{\rm max}$	temperature showing resistance maximum
$T_{\mathbf{N}}$	Néel temperature
TPT	topological phase transition
$T_{\rm sf}$	spin fluctuation temperature
U	internal energy
V	volume of unit cell
V_0	volume at ambient pressure
-	*

1. INTRODUCTION

The physical properties of condensed matter are dominated by interactions between particles or quasiparticles. Among them, the electron correlations are the most important interactions in determining the electronic and magnetic properties of condensed matter. In other words, the understanding of the mechanisms of electron correlations in condensed matter is one of the most basic problems in solid-state physics. High- T_c superconductivity (SC) and novel physical properties of rare earth compounds are thought to originate from strong electron correlations in f- and d-electron systems. In alloys and intermetallic compounds, including rare earth elements, many anomalous physical properties such as Kondo effect, magnetic ordering, SC, and other have been observed. These phenomena are closely connected to the electron correlations between localized 4f electrons and conduction electrons.
It has been well known that physical properties of materials on the border of magnetic instability are strongly dependent on external parameters such as external pressure, magnetic fields, and chemical composition. Novel electronic properties of rare earth compounds are due to the existence of localized 4f electrons, which generally speaking, have strong electron correlations and unstable electronic states. These properties are also expected from the anomalous pressure–temperature phase diagram of rare earth elements, in which numerous phase transitions are observed at low temperature and at high pressure. The heavy fermion (HF) compounds, which are a group of Kondo compounds that have extremely large specific heat coefficients, are typical examples having unstable electronic states, and it is well known that their physical properties are affected strongly by a change of magnetic field and external pressure.

In this chapter, we present the structural and thermal properties of rare earth compounds under high pressure in connection with their electronic and magnetic properties. Pressure is an excellent tool facilitating many types of phase transitions, including quantum phase transitions (QPTs) in condensed matter. There is a large body of research describing physical properties of condensed matter under high pressure in relationship not only to magnetic and electronic properties but also to structural properties. Because of size constrains, we confine our discussion to the present status of research in thermal and electronic aspects of physical properties of rare earth compounds, in which almost all examples are or may potentially be highly correlated compounds including rare earth elements. Further, we hope that this review may give important suggestions to future rare earth research. In the following four sections, we will summarize the experimental results known to date and explore the new trends in this research area.

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2. STRUCTURAL STUDIES OF RARE EARTH COMPOUNDS USING DIFFRACTION TECHNIQUES UNDER HIGH PRESSURE

In this section, we show some examples of structural phase transitions of intermetallic compounds containing rare earth elements that show Kondo effect. The volume and the valence of rare earth elements are often changed through a change in the characteristic temperature, the so-called Kondo temperature $T_{\rm K}$, which is influenced significantly by applying

pressure. The electronic states and the physical properties such as elastic or lattice properties are closely related to each other in Kondo compounds.

2.1 X-ray diffraction

2.1.1 GdCu

It is well known that Murnaghan's equation is applicable for a wide range of materials, and the elastic constants are sensitive to the electronic state. As example of rare earth compound, we show first the data of non-Kondo GdCu. GdCu show a structural phase transformation from the cubic CsCl-type to the FeB-type structure at low temperature (Blanco et al., 1999; Van Dongen et al., 1983). This transformation is known as a diffusionless martensitic transition, in which a large thermal hysteresis is observed with large volume and electrical resistivity anomalies (Ohashi et al., 2003b). The structural study was carried out by using high-pressure X-ray diffraction, which was performed by Rodríguez et al. (2007) at room temperature up to 11 GPa. It was found that the CsCl structure is stable in the whole range of pressures. The evolution of the cell volume with pressure is plotted in Figure 1. It is seen that the change of volume is smooth against pressure. In order to estimate the bulk modulus, a least-square fit of the data to the following Murnaghan's equation of state was employed:

$$\frac{V}{V_0} = \left[\frac{B_0'}{B_0}P + 1\right]^{-1/B_0'}.$$
(1)



FIGURE 1 Relative volume of GdCu as a function of pressure (Rodríguez et al., 2007).

Here, B_0 is the bulk modulus and B_0' is its pressure derivative. The solid line in Figure 1 shows the result of fitting, in which the observed data are well reproduced. The obtained values are $V_0 = 42.68 \text{ Å}^3$, $B_0 = 69.7 \text{ GPa}$, and $B_0' = 3.97$. It is interesting to note that the initial compressibility is very close to the average compressibility of Gd and Cu elements. The authors suggested possible crystal structural transformation above 11 GPa to a low-symmetry structure. This result confirms the hypothesis of Degtyareva et al. (1997) in which the existence of an orthorhombic structure with the AuCd-type at high pressure has been proposed.

2.1.2 Structural transitions in CeX_m Kondo compounds

These compounds show interesting electronic properties depending on *m*. First, we consider the Kondo compound with m = 1 that has the CsCl-type structure CeZn, and then we show the case of m = 6 and a HF Kondo compound CeCu₆.

2.1.2.1 CeZn Kondo compound CeZn is an antiferromagnet with $T_{\rm N} = 30$ K, where a cubic to tetragonal phase transition occurs (Pierre et al., 1981). Kadomatsu et al. (1986) reported a pronounced enhancement of the Kondo anomaly, an antiferromagnetic transition and a structural phase transition by applying high pressure. The magnetic and crystallographic structures of CeZn single crystal were studied by Shigeoka et al. (1990) using neutron diffraction (ND) under pressure up to 1.2 GPa and below 60 K. X-ray diffraction study of CeZn at high pressure was carried out by Uwatoko et al. (1992b). The pressure dependence of the (110) peak position is shown in Figure 2. Bragg angle increases smoothly with increasing pressure, which indicates a decrease in lattice constant. Above 3 GPa, however, the (110) peak splits into two peaks (001) and (110), whereas the (001) and (002) peaks do not. This result indicates that the crystal structure changes from cubic to rhombohedral structure above 3 GPa as was found in previous ND measurement (Kadomatsu et al., 1986; Shigeoka et al., 1990).

The pressure variation of the axial angle β of the rhombohedral cell is shown in Figure 3 (Uwatoko et al., 1992b). The authors could not determine whether the cell expands or shrinks along the [111] direction. Here, they assumed that the cell expands. From the results of Figures 2 and 3, the structural phase transition takes place at P = 2.6 GPa at room temperature. This value is in good agreement with that estimated on the basis of previous phase diagram which is shown in Figure 4: the boundary between the cubic and rhombohedral structures is extrapolated to room temperature, and they got P = 2.6 GPa as a transition pressure.

Figure 5 shows the change of unit cell volume *V* of CeZn as a function of pressure at room temperature up to 10 GPa (Uwatoko et al. 1992b). The volume *V* is calculated by the following relation $V = a^3(1 - 3\cos^2\beta + 2)$



FIGURE 2 The pressure dependence of the (110) peak position (Bragg angle is given as 8θ) for CeZn at room temperature (Uwatoko et al., 1992b).



FIGURE 3 The pressure dependence of the axial angle β of the rhombohedral cell (Uwatoko et al., 1992b).

 $\cos^3\beta$)^{1/3}, where *a* and β are the lattice constants. *V* decreases approximately linearly with increasing pressure. A discontinuity change is not observed within the experimental error in the pressure–volume relation due to first-order structural transition. The volume compressibility is estimated to be $\kappa = -(1/V)(\partial V/\partial P) = 1.71 \times 10^{-2} \text{ GPa}^{-1}$, which is comparable with those of other magnetic Kondo compounds, for example, CeAg ($1.98 \times 10^{-2} \text{ GPa}^{-1}$; Takke et al., 1980) and CeIn₃ ($1.30 \times 10^{-2} \text{ GPa}^{-1}$; Oomi et al., 1986). Considering these facts and that



FIGURE 4 Magnetic and structural pressure-temperature (P-T) phase diagram for CeZn. The solid circles represent the data reported by Shigeoka et al. (1990).



FIGURE 5 Pressure dependence of the unit cell volume *V* of CeZn at room temperature (Uwatoko et al., 1992b).

there is no trace of volume anomaly in the compression curve, like $\gamma - \alpha$ transition in Ce, the valence of Ce in CeZn may be 3+ at least up to 10 GPa at room temperature. In other words, no valence transition, which has been observed in several Kondo compounds, is induced by high pressure up to 10 GPa at room temperature.

2.1.2.2 CeCu₆ CeCu₆ has an orthorhombic crystal structure at ambient pressure and is a typical HF material that has a very large effective electron mass, which is about 1000 times greater than that of free electron (Stewart, 1984). It has been reported that the crystal structure changes from orthorhombic to monoclinic around 200 K ($=T_m$) at ambient pressure (Asano et al., 1986; Gratz et al., 1987). Although this phase transition does not appear in the temperature dependence of electrical resistance, it is observed in the measurements of elastic constants (Suzuki et al., 1985), neutron scattering (Noda et al., 1985), and lattice constants (Bauer et al., 1987). Goto et al. (1988) revealed that the elastic constant C_{66} showed a complete softening around T_m ; further, T_m decreases with increasing pressure up to 0.4 GPa. The X-ray diffraction study was carried out both at room temperature and at liquid nitrogen temperature (Oomi et al., 1988a; Shibata et al., 1986). Figure 6 shows the lattice constants *a*, *b*, and *c* as a function of pressure up to about 10 GPa at room temperature. It is found that *a* is almost constant against pressure, while *b* and *c* decrease smoothly with increasing pressure, indicating a large anisotropy in lattice compression. The linear compressibility κ_i (*i* = *a*, *b*, or *c*) is estimated by using the compression curves. κ_a is extremely small and the values of κ_b and κ_c are 4.8 \times 10⁻³ and 4.2 \times 10⁻³ GPa⁻¹, respectively. In other words, the *b*-axis is more compressible than the *c*-axis. It is concluded that there is



FIGURE 6 Lattice constants of CeCu₆ as a function of pressure at room temperature (Oomi et al., 1988a).

no crystal structure change and no volume anomaly at room temperature under high pressure at least up to 10 GPa.

The crystal structure of CeCu₆ has been reported to transform from orthorhombic to monoclinic around 200 K at ambient pressure, which cannot be observed by electrical resistivity measurement (Shibata et al., 1986). Figure 7 shows the pressure dependence of a, b, and c at 77 K. In the course of the data analysis at 77 K, the orthorhombic structure was assumed because the angle between *a* and *c* axes, β , is nearly 90° (Asano et al., 1986). The value of a is almost independent of pressure, which is similar to room temperature data. The pressure dependences of *b*- and *c*axes can be approximated by two straight lines within experimental errors, with a break of slope around 4.5 GPa. This fact indicates that a phase transition takes place near 4.5 GPa at 77 K. The *b*- and *c*-axes below 4.5 GPa are more compressible than above 4.5 GPa. From Figure 7, κ_b at 77 K is larger than κ_c . Further, the values of κ_b and κ_c below 4.5 GPa are found to be larger than those above 4.5 GPa, which indicates that the highpressure phase (hpp) above 4.5 GPa is harder than the low-pressure phase (lpp) below 4.5 GPa. The bulk moduli were roughly estimated to be B (hpp) = 200 GPa and B(lpp) = 100 GPa.

We now consider the anomaly in the lattice compression observed at 77 K around 4.5 GPa. The $T_{\rm m}$ of CeCu₆ was reported to decrease with increasing pressure with a rate of $\partial T_{\rm m}/\partial P = -20$ K GPa⁻¹ (Suzuki et al., 1985). Considering this result and $T_{\rm m} = 168$ K at ambient pressure, we obtain a speculative *P*–*T* phase diagram, which is shown in Figure 8 (Oomi et al., 1988a). It is surprising that the point (T = 77 K, P = 4.5 GPa) falls on the line which is extrapolated from the data mentioned above. In other word, the anomaly is considered to correspond to



FIGURE 7 Lattice constants of CeCu₆ as a function of pressure at 77 K (Oomi et al., 1988a; Shibata et al., 1986).



FIGURE 8 Speculated pressure-temperature phase diagram of CeCu₆ (Oomi et al., 1988a).

the monoclinic–orthorhombic phase transition induced by pressure at 77 K. Further, the present result is confirmed to be consistent with that obtained by alloying with La (Ōnuki et al., 1985).

Finally, we consider the origin of the large bulk modulus observed in hpp at 77 K. There have been several investigations of elastic anomalies of rare earth alloys and compounds (Lavagna et al., 1983; Neumann et al., 1982, 1985). It was shown that the magnitude of longitudinal mode C_{11} of CeCu₆ decreases around T_m . The difference in the magnitude of C_{11} between the two phases is about 0.1%. Since the bulk modulus of hpp is larger than that of lpp by several tens of percent, the structural change is not the main origin of the large bulk modulus in hpp. Neumann et al. (1982) showed that there is a linear relationship between bulk modulus and the valence. According to their empirical relation, a valence change of 0.3 is estimated to correspond to an increase of several tens of gigapascal in the magnitude of *B*. Further, it should be noted that the lattice constants of α -Ce, which is stable above 5 GPa at room temperature is almost independent of pressure below 9 GPa (Franceschi and Olcese, 1969).

This fact implies that the bulk modulus of α -Ce is extremely large. Taking these facts into account, the Ce atom in the hpp of CeCu₆ may be in the same electronic state as in α -Ce which is considered as the mixed-valence state material. Thus the large bulk modulus may be originated mainly from a valence change of Ce atom induced by pressure. This consideration is supported by the pressure-induced electronic crossover as was observed in the electrical resistance measurements (Oomi et al., 1993b).

2.1.3 Continuous valence transition under pressure

In this section, we show an interesting electronic state observed in some Ce compounds, that is, intermediate (or mixed) valence state, which is induced by applying pressure. This electronic transition or electronic crossover may be related to Kondo states that have very high $T_{\rm K}$. In Section 4, we will show that $T_{\rm K}$ of Kondo compounds is strongly influenced by applying pressure since the magnitude of hybridization between conduction electrons and 4f electrons changes significantly at high pressure (Oomi et al., 1993b). In other words, we can induce a valence transition by controlling the magnitude of $T_{\rm K}$. It should be noted that this type of transition is usually accompanied by a continuous change in volume.

2.1.3.1 CeAl₃ CeAl₃ has the Ni₃Sn-type hexagonal structure and is a prototype HF compound, in which a large value of specific heat coefficient γ and an extremely large value of T^2 term in the electrical resistivity have been found (Andres et al., 1975). These properties are affected significantly by applying pressure. At high pressure, this compound shows a crossover from HF (small T_K) to intermediate valence (IV) (large T_K) states through the increasing T_K . The details about this crossover will be mentioned in Section 4.1.1.

Figure 9 shows the fractional change of lattice constants *a* and *c* along with the unit cell volume $V = \sqrt{3}a^2c/2$ as a function of pressure (Kagayama and Oomi, 1995). The lattice constants were determined mainly from the reflections (110), (101), and (201) of X-ray diffraction measurement at high pressure. Since no extra diffraction lines were observed, it was assumed that the hexagonal structure is stable at room temperature up to 17 GPa. A discontinuous change in the lattice constant, like for a γ - α transition in Ce metal, is not observed within experimental error. Thus the crossover from concentrated Kondo (CK) to IV state observed in the electrical resistivity of CeAl₃ (Kagayama and Oomi 1996; and see Section 4.1.1) occurs gradually without volume anomaly. To estimate the bulk modulus, a least-squares fit of the volume data to Eq. (1) was attempted. We obtained the following values, $B_0 = 54$ GPa and $B_0' = 3.0$. If Eq. (1) is extended to the negative pressure region, the chemical pressure associated with the substitution of Ce by La is



FIGURE 9 Relative changes of the lattice constants a, c, and the unit cell volume V of CeAl₃ as a function of pressure (Kagayama and Oomi, 1995).

estimated to be -1.7 GPa by using the volume of LaA1₃. The pressure coefficient of electrical resistivity ρ at ambient pressure, $\partial \ln \rho / \partial P = \partial \ln R / \partial P$ $\partial P - 1/3B_0$, is estimated to be 0.186 GPa⁻¹(Kagayama and Oomi, 1995). The volume dependence of ρ , $-\partial \ln \rho / \partial P \times B_0$, is 9.97, which is nearly the same as that of CeInCu₂ (Kagayama et al., 1991a). B_0' is commonly observed to be 3–4 in HF systems. Since B_0' is written as $B_0' = -\partial \ln$ $(BV)/\partial \ln V|_{P=0}$ and BV is considered as cohesive energy per unit cell volume (B has dimension of [energy]/[volume]), B_0' is regarded as a Grüneisen parameter of cohesive energy. The compression is strongly anisotropic reflecting a noncubic crystal structure. To examine the anisotropy in the compression, the axial ratio c/a is plotted in Figure 10 as a function of pressure (Kagayama and Oomi, 1995). It increases with increasing pressure. At ambient pressure $c/a \sim 0.7$ which is approximately half of the ideal close-packed hexagonal value (= $\sqrt{8/3}$), but it tends to show higher symmetry under pressure compared to that at ambient pressure. The solid line is obtained by least-squares fit to the equation



FIGURE 10 The axial ratio c/a of CeAl₃ as a function of pressure (Kagayama and Oomi, 1995).

$$\frac{c}{a} = \frac{c_0}{a_0} \left(\frac{V_0}{V}\right)^{\gamma_1},\tag{2}$$

which is assumed tentatively. We obtained $\gamma_1 = 0.24$. It was found that the magnitude of B_0 (=53.6 GPa) is much smaller than those of other HF materials (e.g., $B_0 = 100$ GPa for CeCu₆ and CeInCu₂), which may suggest an unstable electronic state of CeAl₃ under the influence of external forces.

In order to examine the relation between the electronic state and the lattice compression, we will show the temperature-dependent electrical resistivity under high pressure because it reflects the electronic state more sensitively than lattice compression. The temperature dependence of the electrical resistivity ρ of CeAl₃ at various pressures up to 8 GPa and ρ of LaAl₃ at ambient pressure are shown in Figure 76 in Section 4.1.1 (Kagayama and Oomi, 1996). The ρ of LaAl₃ is similar to the ordinary nonmagnetic metal; it varies linearly with temperature above 100 K without any anomaly. While, at ambient pressure, ρ of CeAl₃ increases logarithmically with decreasing temperature until it reaches a maximum at 35 K and has a shoulder near 6 K. This behavior is due to the Kondo scattering on a thermally populated level split by crystalline electric field (CEF; (Cornut and Cogblin, 1972). With increasing pressure, the peak and the shoulder are merged into one peak, which is shifted toward higher temperatures. The ρ at 8 GPa becomes similar to that of LaAl₃. This result is interpreted as a pressure-induced crossover in the electronic state of CeAl₃ from small T_K HF state to large T_K IV state associated with an increase in the hybridization between conduction electrons and 4f electrons. More details can be found in Section 4.1.1.



FIGURE 11 Pressure dependence of ρ of CeAl₃ at various temperatures (Kagayama, 1995).

Figure 11 is isothermal ρ -*P* curve of CeAl₃ at various temperatures. The ρ at room temperature shows a maximum near 4 GPa(= P_c), which corresponds to the crossover in the electronic state. Above 4 GPa, CeAl₃ is in the IV state. It should be noted that there is no anomaly in the pressure dependence of volume or lattice constants as is seen from Figure 9. This result indicates that the electronic crossover in CeAl₃ occurs without any volume anomaly. The result in Figure 11 shows that $P_{\rm c}$ increases with increasing temperature, which is consistent with the pressure dependence of $T_{\rm K}$ as will be mentioned below. In order to get the temperature-dependent 4f magnetic contribution ρ_{mag} , the ρ of LaAl₃ is assumed to be pressure-independent phonon part of CeAl₃ and subtracted from the ρ data of CeAl₃ at various pressures, $\rho_{mag} = \rho(CeAl_3) - \rho(LaAl_3)$ (Kagayama and Oomi, 1996). In Section 4.1.1, T_{max} is found to increase with increasing pressure. Since T_{max} is roughly proportional to the $T_{K'}$ it may be inferred that $T_{\rm K}$ also increases with pressure. This result is the same as mentioned above.

2.1.3.2 CeRh₂Si₂ and CeAu₂Si₂ In this section, we illustrate some examples of pressure-induced valence transitions in rare earth compounds exhibiting magnetic order. The compounds, CeRh₂Si₂ and CeAu₂Si₂, are selected as typical examples which are antiferromagnetic at low temperature. In CeRh₂Si₂, T_N decreases with increasing pressure, and antiferromagnetism (AFM) disappears at high pressure as will be also mentioned in Section 4.2.1. However, T_N of CeAu₂Si₂ increases with pressure, which is in sharp contrast with CeRh₂Si₂. Considering these facts, we suggest that CeRh₂Si₂ is on the right hand side of the peak of Doniach's phase diagram (1977), but CeAu₂Si₂ is on the left hand side of that the same

diagram. Hence, it is interesting to compare the electronic and lattice properties of these two compounds under high pressure.

CeRh₂Si₂ with the ThCr₂Si₂-type tetragonal structure orders antiferromagnetically below the Néel temperature $T_{N1} = 36$ K. Below $T_{N2} = 24$ K, there occurs a change of the magnetic structure, from the antiferromagnetic state with the propagation vector $q_1 = (0.5, 0.5, 0)$ to the 4q structure (Kawarazaki et al., 2000). CeRh₂Si₂ is considered to be a standard 4f-localized system.

In order to investigate pressure dependence of lattice parameters, X-ray diffraction measurement was carried out (Ohashi et al., 2003a). At ambient pressure, the crystal structure is tetragonal with the lattice parameters a = 4.070 Å and c = 10.156 Å, which are consistent with previous experiments (Settai et al., 1997). Figure 12 shows the pressure dependences of the relative lattice parameters a/a_0 , c/c_0 , and the relative volume V/V_0 as a function of pressure at room temperature, where a_0 , c_0 , and V_0 are the values at the ambient pressure. The tetragonal structure is stable up to 13 GPa at room temperature. Both *a* and *c* decrease with increasing pressure; no discontinuous changes have been observed within experimental error. Linear compressibilities, $\kappa_i = (-1/i)(\partial i/\partial P)$, i = a or c, of *a*- and *c*-axes are 2.2×10^{-3} and 3.0×10^{-3} GPa⁻¹. The *c*-axis is more compressible than the *a*-axis. We attempted a least-squares fit of the data of V/V_0 to the first-order Murnaghan's equation of state Eq. (1). The results are shown in Figure 12 as a solid line for V/V_0 . The agreement between the observed points and the calculated ones is satisfactory. B_0 and B' are estimated to be 139 GPa and 2.2, respectively.

The temperature dependence of the electrical resistivity along the *a*-axis is shown in Figure 105 in Section 4.2.1 in a wide temperature



FIGURE 12 Pressure dependence of a/a_0 , c/c_0 , and V/V_0 of CeRh₂Si₂. The solid line for the pressure dependence of V/V_0 shows the result of the least-square fitting using Murnaghan's equation. The dashed lines for a/a_0 and c/c_0 are guides to the eye (Ohashi et al., 2003a).

range under pressures up to 8 GPa. No anomalies have been detected in the ρ above 1.5 GPa, since magnetic ordering was suppressed completely. Instead of that, an inflection point at $T_{\rm m}$ is observed in the ρ -T curves above 1.5 GPa. $T_{\rm m}$ is found to shift rapidly from 44 K at 1.5 GPa to higher temperature with increasing pressure. T^2 dependence was observed at low temperature below $T_{\rm m}$. The coefficient A_a of the T^2 term along the *a*-axis decreases significantly with increasing pressure: the value of A_a at 8 GPa is smaller than that at 1.5 GPa by two orders of magnitude. $T_{\rm m}$ is related to Kondo temperature $T_{\rm K}$.

According to the theory of Yoshimori and Kasai (1983), Kondo temperature $T_{\rm K}$ is proportional to $A^{-1/2}$, where A is the coefficient of T^2 term. Then the Grüneisen parameter Γ of $T_{\rm K}$ is written (Kagayama and Oomi, 1996) as

$$\Gamma = -\left[\frac{\partial \ln T_{\rm K}}{\partial \ln V}\right]_{V=V_0} = \frac{1}{2} \left[\frac{\partial \ln A}{\partial \ln V}\right]_{V=V_0} = \frac{V_0}{2} \left[\frac{\Delta \ln A}{\Delta V}\right].$$
(3)

In Figure 13, the values of *A* are plotted on the logarithmic scale as a function of $\Delta V/V_0$. The linear relationship is found in the plot as is shown by solid lines above 1.5 GPa ($\Delta V/V_0 > 0.011$). From this, Γ is estimated to be 42 for CeRh₂Si₂, which is extremely large and comparable with those of other HF compounds, such as 59 and 65 for CeInCu₂ and CeCu₆, respectively (Kagayama and Oomi, 1996). Below 1.5 GPa, on the other hand, the observed value deviates significantly from the linear relation, suggesting that the electronic state is very unstable near the quantum critical point (QCP) near *P*_{c1} (~1 GPa).

Next we consider the electronic state of the intermetallic compound CeAu₂Si₂ under pressure, which also has the ThCr₂Si₂-type tetragonal



FIGURE 13 A_a of CeRh₂Si₂ as a function of fractional change in volume, $\Delta V/V_0$ (Ohashi et al., 2003a).

structure and exhibits an antiferromagnetic order below 8 K. The lattice constants of this compound were measured by using X-ray diffraction under high pressure up to 13 GPa at room temperature (Ohmura et al., 2009). Since there appear no new Bragg peaks in the powder diffraction spectra, the crystal structure of ThCr₂Si₂ is stable at least up to 13 GPa. Figure 14 shows the lattice constants as functions of pressure. It is seen that both the *a* and *c*-axes change smoothly with pressure within experimental errors. The linear compressibilities for a- and c-axes are $\kappa_a = 3.68 \times 10^{-3} \text{ GPa}^{-1}$ and $\kappa_c = 2.69 \times 10^{-3} \text{ GPa}^{-1}$, respectively. This result indicates that the *a*-axis is more compressible than the *c*-axis, that is, the compression is anisotropic, which implies that the cohesive energy is also anisotropic. Figure 15 shows the c/a ratio as a function of pressure. Reflecting the anisotropic compressibilities, the value increases with increasing pressure. The increase of c/a at high pressure has been also reported in other Ce Kondo compounds (Kagayama and Oomi, 1995; Wassilew-Reul et al., 1997).

Figure 16 shows V/V_0 as a function of pressure up to 13 GPa at room temperature, where $V (=ca^2)$ and V_0 are the volumes at high and ambient pressure, respectively. V/V_0 decreases smoothly with increasing pressure below 13 GPa without any anomalies. The bulk modulus was obtained by assuming the Murnaghan's equation (1). By least-square fitting of the experimental data to Eq. (1), we obtained $B_0 = 112$ GPa and $B_0' = 3.2$,



FIGURE 14 The lattice constants a and c of CeAu₂Si₂ as a function of pressure at room temperature (Ohmura et al., 2009).



FIGURE 15 The c/a ratio of CeAu₂Si₂ as a function of pressure (Ohmura et al., 2009).



FIGURE 16 Pressure dependence of relative volume of $CeAu_2Si_2$. The solid curve shows the result of fitting to Eq. (1) (Ohmura et al., 2009).

respectively. The pressure dependence of electrical resistivity at room temperature is illustrated in Figure 17. ρ increases smoothly with pressure below 8 GPa. There are no anomalies in ρ –P curve at room temperature, which is different from those of CeAl₃ and CeAl₂ (Kagayama and Oomi, 1995; Miyagawa et al., 2008 and see the following paragraph).

Figure 18 illustrates the ρ versus temperature of CeAu₂Si₂ at various pressures. ρ has a peak around 8 K and a broad shoulder around 150 K. The low-temperature peak is due to both Kondo effect and magnetic



FIGURE 17 Pressure dependence of electrical resistance of $CeAu_2Si_2$ at room temperature (Ohmura et al., 2009).



FIGURE 18 Temperature dependence of the electrical resistivity of $CeAu_2Si_2$ at various pressures (Ohmura et al., 2009).

ordering. Indeed, the magnetic susceptibility of the present sample shows a rapid drop around 8 K, showing the AFM ordering. The magnitude of the electrical resistivity increases with pressure in the whole temperature range. The peak and the broad shoulder are observed in all ρ –*T* curves at all pressures up to 8 GPa. The shapes of ρ –*T* curves are almost independent of pressure except the magnitude of ρ .

2.1.3.3 CeAl₂ CeAl₂ with the cubic Laves phase MgCu₂ structure is well known as a typical HF compound, which has a large electronic specific heat coefficient $\gamma = 135$ mJ/mol K² (Steglich et al., 1979). Antiferromagnetic order is observed at $T_N = 3.8$ K (Tomisawa et al., 2006), which is due to the formation of spin-density wave (SDW). The Ce ion in CeAl₂ is trivalent at ambient pressure. Kondo temperature T_K and the CEF splitting energies were estimated to be 6 K, $T_1 = 100$ K and $T_2 = 180$ K from the neutron-scattering measurement (Loewenhaupt et al., 1979; Steglich et al., 1979). Although the CEF of cubic Ce compounds of the J = 5/2 ground state should split into a Γ_7 doublet and a Γ_8 quartet, the CEF splitting in CeAl₂ shows three levels. This was explained by assuming existence of a bound (by strong magnetoelastic coupling) state between a crystal-field excitation and a low-lying phonon (Thalmeier and Fulde, 1982).

The pressure dependence of electrical resistivity ρ –P curve of CeAl₂ at room temperature is shown in Figure 85 in Section 4.1.2. It is seen that the resistivity increases with pressure but shows a broad maximum around 6 GPa. This result is explained as a crossover in the electronic state such as the electronic transition from the HF (small $T_{\rm K}$) state to an IV (large $T_{\rm K}$) state (Miyagawa et al., 2008; Oomi et al., 2005). In order to see this phenomenon in more detail, we show the volume and the ρ curves of CeAl₂ under high pressure. Figure 19A and B shows the pressure dependences of V/V_0 and the temperature dependence of electrical resistivity of CeAl₂ at high pressure below 15 and 8 GPa, respectively (Miyagawa et al., 2008). CeAl₂ is well known to show a pressure-induced continuous valence transition (Barbara et al., 1986), which is reflected in the ρ -T curves under high pressure. At ambient pressure, the electrical resistivity shows typical CK properties such as log T dependence followed by magnetic ordering. The ρ at 3 GPa has a broad peak at low temperature but it disappears at 8 GPa, in which ρ shows a smooth increase with increasing temperature same as that of normal metals. The Kondo temperature T_K of CeAl₂ at ambient pressure is 6 K, but it increases with pressure and becomes around 290 K at 5.5 GPa. So the ρ at 8 GPa shows a smooth temperature dependence similar to that of large $T_{\rm K}$ (or IV) Kondo compounds. Such correspondences between ρ curves at high pressure and valence changes have been observed in many Kondo compounds (Kagayama and Oomi, 1996; Oomi et al., 1993b).

From the result described in Figure 18, it should be noted that the shape of ρ -*T* curve of CeAu₂Si₂ is not affected strongly by pressure up to 8 GPa. This is in sharp contrast with those of CeAl₂ and other Kondo compounds (Kagayama and Oomi, 1996; Kagayama et al., 1991a; Miyagawa et al., 2008), in which the ρ -*T* curves are affected significantly by applying pressure as shown in Figure 80 in Section 4.1.2 and Figure 19B. Considering these facts, the valence change in CeAu₂Si₂



FIGURE 19 (A) Pressure dependence of cell volume in $CeAl_2$ and (B) electrical resistivity at high pressure (Miyagawa 2008).

occurs slowly compared to other Ce Kondo compounds. Further, $T_{\rm K}$ of CeAu₂Si₂ (~8 K roughly estimated from the peak in ρ) seems not to increase so much by applying pressure. In other words, the Kondo state in CeAu₂Si₂ is stable at high pressure.

Usually, the electronic states of Kondo compounds have been discussed on the basis of the Doniach's phase diagram (Doniach 1977; Brandt and Moshchalkov, 1984, about the details of this diagram, see Figure 52 in Section 3.4.2), in which the pressure dependence of T_N plays an important role in determining where the material exists in this diagram. From the pressure dependence of T_N , it is suggested that CeAu₂Si₂ is on the left hand side and near the top of the peak of this phase diagram (Link and Jaccard, 1997; Thompson et al., 1986). On the other hand, since CeAl₂ is on the right hand side of the same diagram and is located near the border of the critical pressure, AFM of CeAl₂ disappears at high pressure and a quantum critical transition is observed at moderate pressure (Miyagawa et al., 2008).

The lattice compression of Ce Kondo compounds has been reported by many authors (Kagayama et al., 1990; Vedel et al., 1986). For example, the pressure dependence of volume of CeRh₂Si₂ was reported (Ohashi et al., 2003a), in which the value of V/V_0 changes continuously with pressure. Taking the ρ -T curves at high pressure into account, this compound is considered to show a continuous valence transition having $B_0 = 139$ GPa and $B_0' = 2.2$.

The values of B_0 and B_0' for typical Ce Kondo compounds are summarized in Table 1. It is seen that the values of B_0 are strongly dependent on the nature of the compound. However, the values of B_0' show a systematic behavior. The B_0' is between 2 and 3 for the Ce Kondo compounds showing pressure-induced continuous valence transition (Kagayama and Oomi, 1996). In this sense, CeAu₂Si₂ is classified as a Kondo compound showing pressure-induced valence transition, which may occur very slowly.

There have been quite a number of discrepancies in the compression curves of CeAl₂. A discontinuous change in the pressure dependence of lattice constant at room temperature was observed by some authors (Bartholin et al., 1980; Croft and Jayaraman, 1979) around 6 GPa. But other authors did not find it below 20 GPa (Barbara et al., 1986; Vedel et al., 1986). The origin of these discrepancies seems to be a complicated issue, but it may originate mainly from the lattice compression at nonhydrostatic condition by solidification of pressure medium.

The measurement of X-ray powder patterns of $CeAl_2$ under pressures up to 24 GPa was carried out by using conventional Mo K α X-ray source and helium gas as the pressure-transmitting medium in order to achieve the best possible hydrostatic condition (Miyagawa, 2008). Figure 20 shows the diffraction patterns of $CeAl_2$ below 24 GPa. They are the same as that at the ambient pressure, indicating that the MgCu₂-type structure is stable up to 24 GPa. The pressure dependence of volume *V* at room temperature

Compound	Tκ	T _N	B _o (GPa)	<i>B</i> ₀ ′	Valence transition from $ ho(au)$ curve
CeAu ₂ Si ₂	8	8(6.6–10)	112	3.3	Moderate
CeRh ₂ Si ₂	100	36, 24	139	2.2	Yes
CeAl ₃	5	_	54	3.0	Yes
CeAl ₂	6	3.8	66	3.3	Yes

TABLE 1 B_0 and B_0' for several Ce Kondo compounds (Kagayama and Oomi, 1998; Ohashi et al., 2003a; Ohmura et al., 2009)



FIGURE 20 X-ray diffraction patterns of $CeAl_2$ at room temperature under high pressures by using helium gas as the pressure-transmitting medium. Indices are shown for several resolved Bragg peaks (Miyagawa, 2008).

as a function of pressure is shown in Figure 21. It is found that within experimental error, *V* decreases continuously with increasing pressure below 17 GPa, which is in agreement with the results obtained by the latter group mentioned above. But an anomaly exists near 17 GPa in the compression curves, where the rate of decreasing of the lattice constant becomes lower in the range, 17 < P < 20 GPa. The solid curve is the result of a least-square fit to Eq. (1). The similar diffraction experiment was also done up to 30 GPa by using helium gas and the synchrotron X-ray source and shown in Figure 21. In this experiment, the discontinuous change around 6 GPa was also not observed. However, the same anomaly around 17 GPa was confirmed again.

It has been reported that the anomaly in the compression curve of Zn is induced by the nonhydrostaticity associated with the solidification of the



FIGURE 21 Summary of pressure dependence of volume of $CeAl_2$ and $LaAl_2$. The solid lines are the result of fitting to Eq. (1) (Miyagawa, 2008).

pressure medium (Takemura, 1999). In the case of CeAl₂, however, the anomaly around 17 GPa is observed in all of the compression curves obtained by using both the 4:1 methanol:ethanol mixture and helium gas, which was used to generate the ideal hydrostatic condition. It means that the anomaly must exist, and it is not caused by artifacts related to nonhydrostatic conditions. It is well known that if the variation of an external parameter like pressure gives rise to a change in the Fermi surface topology, it is likely to have an influence on the monotonic variation of the density of states (DOSs) (Lifshitz, 1960). The band structure calculations for CeAl₂ have been performed, and it was suggested that the electronic transition due to a change in the Fermi surface topology (topological phase transition, TPT) brings about the anomaly in the pressure dependence of volume around 15 GPa (Chandra Shekar et al., 1999). This result is in a qualitative agreement with the experimental data shown in Figure 21.

As a reference, the high-pressure X-ray diffraction measurements of LaAl₂ were also performed. The MgCu₂ structure is stable up to 30 GPa, and the compression curve shows a smooth change without any anomalies as also seen in Figure 21. This result indicates that the origin of the anomaly in the compression curve of CeAl₂ observed around 17 GPa is due to the presence of 4f electrons in the cerium-based compound.

The bulk modulus was obtained by assuming the Murnaghan's equation of state, Eq. (1). By least-square fitting of the experimental data to Eq. (1) below 15 GPa, the values of B_0 and B_0' were obtained, and these are listed in Table 2. The B_0 of LaAl₂ is larger than that of CeAl₂. Similarly, B_0' of CeAl₂ is smaller than that of LaAl₂, which is due to pressure-induced continuous valence transition manifested as an anomalous softening of

Compound	a (Å)	B _o (GPa)	B ₀ ′	X-ray radiation source
CeAl ₂ (1)	8.058	62	3.0	Mo Kα, rotating anode
$CeAl_2(2)$	8.057	61	3.0	PF (BL-18C)
LaAl ₂	8.147	69	3.5	PF (BL-13A)

TABLE 2 B_0 and B_0' (see Eq. (1)) for CeAl₂ and LaAl₂ (Miyagawa et al., 2008)

PF means Photon Factory in High-Energy Accelerator Research Organization, Tsukuba.

the lattice of CeAl₂, as has been revealed by the comparison with the normal trivalent compound LaAl₂ (Barbara et al., 1986; Vedel et al., 1986). The behavior of the compression curve of CeAl₂ above 20 GPa exhibits a tendency to be similar to that of LaAl₂ above 20 GPa. In other words, the continuous valence transition may be suppressed above 17 GPa.

In order to clarify the origins of anomaly in the compression curve of CeAl₂, the electrical resistance of CeAl₂ was measured up to 23 GPa at room temperature using diamond-anvil cell under quasi-hydrostatic condition. According to the result obtained by cubic-anvil-type pressure device, the $\rho(P)$ increases with increasing pressure up to 5.5 GPa, and then decreases as shown in Figure 19B. The maximum is explained to be due to the Kondo effect, where the Kondo temperature $T_{\rm K}$ (which is around 6 K at ambient pressure) increases with pressure and then reaches room temperature around 5.5 GPa, that is, the pressure-induced crossover occurs in the vicinity of 5.5 GPa at room temperature.

Figure 22 shows the electrical resistivity at room temperature as a function of pressure up to 23 GPa. It is found that the $\rho(P)$ continues to decrease with increasing pressure up to 15 GPa and then becomes constant above 17 GPa. Considering the result shown in Figure 85 in Section 4.1.2 as pressure increases, the electrical resistivity of CeAl₂ at room temperature increases, then shows a maximum around 5 GPa ($=P_{max}$), and finally decreases up to 15 GPa. The pressure of 17 GPa where the behavior of $\rho(P)$ changes is in good agreement with the anomaly in the compression curves shown in Figure 21. Thus, the anomaly around 17 GPa is observed in both pressure dependence of the lattice constant and the electrical resistivity. This fact suggests that the anomaly at 17 GPa is related to a change in the electronic state of the compound.

As mentioned above, CeAl₂ is well known to show a pressure-induced continuous valence transition, which is considered to still exist around 17 GPa. But since the compression curve of CeAl₂ above 17 GPa becomes similar to that of LaAl₂, the valence transition is expected to be suppressed or becomes negligible above 17 GPa. AuIn₂ is another typical example of a compound that shows pressure-induced TPT. It has been reported (Godwal et al., 1998) that AuIn₂ shows anomalies in the pressure



FIGURE 22 Pressure dependence of the electrical resistivity of $CeAl_2$ up to 23 GPa at room temperature (Miyagawa, 2008).

dependence of electrical resistance and fusion curve at 2–3 GPa. The electrical resistance decreases rapidly below 2 GPa, but the slope becomes small above 2 GPa. On the basis of the band structure calculation, Godwal et al. attributed this transition to be Lifshitz singularity or TPT. The change in slope of $\rho(P)$ curve around 17 GPa observed in CeAl₂ is similar to that in AuIn₂. Further, the TPT in AuIn₂ was confirmed to occur without any structural change. This is also similar to CeAl₂.

Judging from these facts, it is suggested that the anomaly around 17 GPa is brought about by a combined effect of TPT and the continuous valence transition which may be related to a change in the Fermi surface topology.

2.2 Neutron diffraction under high pressure

2.2.1 Micro-pressure cell

In neutron-scattering experiments using piston-cylinder cells, neutrons penetrate not only the material studied but also the surrounding pressure-transmitting medium and materials used to construct the pressure cells. Therefore, it is important to know the neutron transmission properties of these materials. Neutron transmission coefficients of various alloys use in manufacturing pressure cells are shown as a function of neutron energy in Figure 23. For example, only 9% of neutrons at a typical energy of 14.8 meV penetrate the MP35N alloy with thickness of 10 mm, while about 30% and 40% of neutrons will penetrate the NiCrAl and CuBe alloys with



FIGURE 23 Neutron transmission properties of various alloys that are used in manufacturing pressure cells represented as a function of neutron energy.

the same thickness at this energy, respectively. Thus, it appears that NiCrAl and CuBe alloys are most suitable materials for making pressure cells.

The neutron transmission properties of various pressure-transmitting media were also studied as a function of neutron energy. In general, hydrogen-free Fruorinert and deuterated alcohol systems are both suitable for neutron transmission. Therefore, one can use Fluorinert FC75, mixtures of FC84/87 and other, or deutrated methanol/ethanol mixtures suitable for the pressure range studied after taking into account the hydrostatic limit (Angel et al., 2007; Klotz et al., 2009; Osakabe and Kakurai, 2008; Sidorov and Sadykov, 2005).

High-pressure cells used in our experiments were designed for use with a cryostat with the sample space ~65 mm in height and ~30 mm in diameter. Figure 24A shows a schematic drawing of the CuBe cell that has 14 mm external diameter. Hardened CuBe alloy was used for most of the cell to obtain the maximum pressure of 2 GPa (Aso et al., 2006b). As an example of the pressurizing test for the cell, Figure 24B illustrates the pressure dependence of linewidths of Q = (2, 0, 0) Bragg reflections of single-crystalline NaCl, where a Fluorinert FC75 was used as a pressure-transmitting medium. The pressure was estimated by determining the change in the lattice parameter of NaCl (Skelton et al., 1984). The rocking curve linewidth is constant up to ~0.3 GPa, and it increases at higher pressure. The radial scan linewidths, which roughly measures the pressure distribution in the cell, are unchanged within the accuracy of a few percent



FIGURE 24 (A) Schematic drawing of the pressure cell. Hardened CuBe alloy is used for a cylinder. (B) FWHM of Bragg profiles at Q = (2, 0, 0) for single-crystalline NaCl as a function of pressure. The lines are guides to the eye (Aso et al., 2006b).

up to 1.3 GPa and then slowly increases. These findings indicate that the hydrostatic limit is near the critical pressure of P = 1.3 GPa for FC75.

A smaller CuBe cell of 8.8 mm external diameter was also designed on the basis of the former cell (Uwatoko et al., 2005), which is more useful for ND studies of neutron absorber materials. For ND at pressures above 2 GPa, a hybrid CuBe/NiCrAl cell was also developed. Its detailed design and other features were reported by Aso et al. (2007). In the following two sections, we will review the applications of the present apparatus to study the magnetic properties of UGe₂ and CeRhIn₅.

2.2.2 UGe₂

UGe₂ is a ferromagnet crystallizing in the orthorhombic ZrGa₂-type structure (space group *Cmmm*) and exhibits pressure-induced SC (Huxley et al., 2001; Saxena et al., 2000). By using the 14-mm Cu–Be cell, a single crystal of UGe₂ can be successfully pressurized up to 1.6 GPa at low temperature (Aso et al., 2006a,b). Figure 25A shows the temperature dependence of ferromagnetic Bragg peak intensities at Q = (0, 0, 1) against the temperature *T* measured at various pressures. The temperature–pressure phase diagram determined by these measurements as illustrated in Figure 25B. Curie temperature (*T*_C) is about 52 K at ambient pressure, and it monotonically



FIGURE 25 (A) Temperature dependence of ferromagnetic Bragg peak intensities at Q = (0, 0, 1) against temperature *T* measured at various pressures (Aso et al., 2006a). (B) Phase diagram of UGe₂ determined by ND measurements. Pressure dependences of the obtained parameters Δ and Θ' from the Stoner model are also plotted, which are normalized with respect to their corresponding values at ambient pressure, that is, $\Delta = 39.5$ K and $\Theta' = 83.4$ K. Characteristic temperatures T_x taken from Tateiwa et al. (2001) are also plotted. The solid lines are guides to the eye (Aso et al., 2006b).

decreases with increasing pressure. The characteristic temperature T_{x} , where a steep increase in the ferromagnetic Bragg peak intensities is observed, also decreases with increasing pressure from ~30 K observed at ambient pressure, and it becomes suppressed to zero at a critical pressure P_x of ~1.2 GPa. In Figure 25B, the pressure dependence of Δ and Θ' parameters obtained from the Stoner model (1938) is also plotted; the Stoner model was applied to the temperature dependence of ferromagnetic Bragg peak intensities at Q = (0, 0, 1) below T_x . In the Stoner model, the magnetization (square root of the neutron intensities) is expressed as follows:

$$M = M_0 \Big(1 - \alpha T^{3/2} \exp(-\Delta/\mathrm{T}) \Big), \tag{4}$$

$$\alpha = \frac{3}{4}\sqrt{\pi} \left(\frac{1}{E_{\rm F}}\right)^{3/2}, \quad \Delta = 2E_{\rm F} \left(\frac{\Theta'}{E_{\rm F}} - 2^{-1/3}\right),$$
 (5)

where M_0 indicates the magnetization at zero temperature, Δ is the socalled Stoner gap, E_F is the Fermi energy, and Θ' is the molecular field coefficient. It should be noted that these quantities of Δ , Θ' , and T_x lie on a single line, suggesting that the characteristic temperature T_x is related to the Stoner gap Δ (equivalently Θ') in the heavy quasiparticle band. These observations imply that the perfectly polarized ferromagnetic state is realized below P_x in UGe₂.

2.2.3 CeRhIn₅

CeRhIn₅, which is a member of the Ce*T*In₅ (T = Rh, Ir, and Co) family with a tetragonal HoCoGa₅-type crystal structure, is an ideal model for studying correlations between AFM and SC because its transition temperatures (Néel temperature, T_N , and superconducting transition temperature, T_c) can be controlled by the application of external pressure. At the ambient pressure, CeRhIn₅ displays AFM ordering below $T_N \sim 3.8$ K. As the pressure increases, T_N passes through a maximum of 4.0 K at approximately 0.8 GPa and then vanishes in the vicinity of the characteristic pressure $P_x \sim 1.85$ GPa. At pressures above P_x , pure SC state emerges at $T_c \sim 2.2$ K.

The magnetic structure of CeRhIn₅ at ambient pressure is an incommensurate (IC) spiral helix along the tetragonal *c*-axis characterized by the propagation wave vector $\tau = (0.5, 0.5, \pm \delta)$, where $\delta = 0.297$. The pressure dependence of δ is controversial. Thus, according to Llobet et al. (2004), δ is almost independent of pressure up to 1.63 GPa, while Majumdar et al. (2002) reported that δ exhibits a jump at approximately 1 GPa. To reveal the intrinsic magnetic structure at ambient and high pressures, measurements under hydrostatic pressure are highly needed. By using the 8.8-mm Cu–Be cell, a single crystal of CeRhIn₅ can be successfully pressurized up to 1.48 GPa at low temperature using the pressure-transmitting medium of a 4:1 deutrated methanol/ethanol mixture with the hydrostatic limit of 10 GPa (Aso et al., 2009). Note that the signal-to-background ratio in the present experiment (~0.75 GPa) is much better than those in the literature (Llobet et al., 2004; Majumdar et al., 2002; Raymond et al., 2008). With increasing pressure, δ gradually increases to 0.326 at 1.48 GPa, exhibiting no anomaly near 1 GPa in contrast to the results obtained by Majumdar et al. (2002). This discrepancy may originate from the difference in the pressure-transmitting media, since Fluorinert used in the previous experiments has a hydrostatic limit of approximately 1 GPa.

To obtain a clear picture of the relationship between AFM and SC in CeRhIn₅, the magnetic structure above and below T_c at P = 1.48 GPa was investigated. Figure 26A illustrates ND profiles along the (0.5, 0.5, l) vector at T = 2.0 K ($>T_c$), 0.90 K ($\sim T_c$), and 0.75 K ($<T_c$). Figure 26B shows the T dependence of the peak intensities at $Q_1 = (0.5, 0.5, 1.326)$ and $Q_2 = (0.5, 0.5, 1.391)$. Upon lowering the temperature, the peak intensity at Q_1 starts to increase at $T_N \sim 3.0$ K and then gradually decreases below the characteristic temperature $T_x \sim 1.6$ K before sharply



FIGURE 26 (A) Neutron diffraction profiles of CeRhIn₅ measured under $P \sim 1.48$ GPa at (top) T = 2.0 K ($> T_c$), (middle) 0.90 K ($\sim T_c$), and (bottom) 0.75 K ($< T_c$). (B) T dependence of the peak intensities at $Q_1 = (0.5, 0.5, 1.326)$ (triangles) and $Q_2 = (0.5, 0.5, 1.391)$ (circles). The intensities of the paramagnetic state are subtracted. The solid line is a guide to the eye (Aso et al., 2009).

dropping at $T_c \sim 0.90$ K. The intensity at 0.75 K is as small as the background level. Interestingly, the peak at Q_2 exhibits the opposite behavior. The intensity at 0.75 K is almost the same as that of Q_1 at T_x . We found that the incommensurability δ exhibits a drastic change at approximately 1 K, which is close to T_c , at 1.48 GPa, that is, the switching of the magnetic ordering occurs. This unexpected behavior suggests the possibility that the AFM order is affected by the SC state.

3. THERMAL PROPERTIES UNDER HIGH PRESSURE

3.1 General survey

The measurements of thermal properties such as specific heat and thermal expansion have been well known to give a lot of important information to understand the physical properties of condensed matter. In particular, one can calculate the effective mass of conduction electrons from specific heat measurement, which plays an important role in determining whether the compound is a heavy electron system or not. However until now, the measurements of physical properties at high pressure have been mainly limited to electrical resistance, magnetic susceptibility, and X-ray (neutron) diffraction. Although specific heat and thermal expansion measurements, including magnetostriction (MS), are complementary techniques compared to magnetic and electric ones, there have been only a few reports of the measurements of the thermal properties of rare earth compounds under high pressure. The main reasons for that are the technical difficulties in the measuring thermal properties under high pressure. Recently, special techniques for measuring the thermal properties under high pressure have been developed extensively. In this chapter, the thermal properties, specific heat and thermal expansions, of rare earth compounds under high pressure are described. First, we provide a brief survey of the physical background of the measurements. Then we report typical measuring techniques of specific heat and thermal expansion under high pressure and finally introduce some examples mainly for highly correlated electron systems such as HF materials and valence fluctuating materials. The section ends with a brief discussion.

3.1.1 Specific heat

According to the classical statistical mechanics, at sufficiently high temperature, specific heat of a solid approaches a constant value C = 3R, also known as the Dulong–Petit limit. It is also well known experimentally that specific heat decreases with decreasing temperature. Generally, the specific heat of a solid is extremely small at low temperature, and it can be represented as $C = \gamma T + \beta T^3$, where, γ and β are constants. The physical meaning of these constants is clarified as follows.

The thermal energy of phonons per unit volume can be described as

$$u = \frac{1}{V} \sum_{\overrightarrow{k},\omega} \left(\left\langle n_{\overrightarrow{k}s} \right\rangle + \frac{1}{2} \right) \hbar \omega_{s} \left(\overrightarrow{k} \right).$$
(6)

And the average number of phonons is given by $\langle n_{\overrightarrow{k}} \rangle = 1/\exp(\hbar\omega_{\rm s}(\overrightarrow{k})/k_{\rm B}T) - 1$, where $\omega_{\rm s}$ is angular frequency, $k_{\rm B}$ is Boltzmann constant, and *T* is absolute temperature.

Specific heat can be defined as

$$C_V = \frac{\partial U}{\partial T} \bigg|_V.$$
(7)

Thus, one can obtain the following description:

$$C_{V} = \frac{1}{V} \frac{\partial}{\partial T} \sum_{k} \frac{\hbar \omega_{s}(\vec{k})}{\exp(\hbar \omega_{s}(\vec{k})/k_{B}T) - 1}.$$
(8)

At high temperature, $k_{\rm B}T >> \hbar\omega_{\rm s}(\vec{k})$, and therefore, the value of the Dulong–Petit limit can be reproduced. In the Debye model, lattice vibrations are approximated as a continuous elastic body considering only acoustic modes, and therefore, phonon spectrum is treated linearly. In other words, $\omega_{\rm s} = v_{\rm s} \vec{k}$. In addition, it is assumed that the speed of sound $(v_{\rm s})$ does not depend on the branch of each mode,

$$C_{V} = \frac{\partial}{\partial T} \sum_{\vec{k}} \int \frac{d\vec{k}}{(2\pi)^{3}} \frac{\hbar \upsilon \vec{k}}{\exp\left(\hbar \upsilon \vec{k} / k_{\rm B} T\right) - 1}.$$
(9)

By replacing the wave vector with the volume of a sphere same as that of the first Brillouin zone, one can obtain specific heat of phonons as follows:

$$C_V = \frac{12\pi^4}{5} n k_{\rm B} \left(\frac{T}{\Theta_{\rm D}}\right)^3 = \beta T^3.$$
(10)

Here, $\Theta_{\rm D}$ is called the Debye temperature and it is given by $\Theta_{\rm D} = \hbar \omega_{\rm D} / k_{\rm B}$.

Debye temperatures of hard materials are generally high. In specific heat measurements at high pressure; however, Teflon cells and various pressure media are common. One has to realize that the latter are soft materials and their Debye temperature changes easily by applying pressure. The result is the corresponding change of their specific heat. These soft materials make specific heat measurement at high pressures difficult. The linear term (γ) in the specific heat expression can be calculated considering Fermi–Dirac distribution function. The energy *u* at arbitrary temperature and the electronic DOSs at the Fermi level *n* can be described as follows:

$$u = \int_0^{\varepsilon_{\rm F}} ED(E) dE + \frac{\pi}{6} (k_{\rm B}T)^2 (\varepsilon_{\rm F}D'(\varepsilon_{\rm F}) + D(\varepsilon_{\rm F})), \tag{11}$$

$$n = \int_0^{\varepsilon_{\rm F}} D(E) dE + \frac{\pi}{6} (k_{\rm B}T)^2 D'(\varepsilon_{\rm F}).$$
(12)

Here, $\varepsilon_{\rm F}$ is Fermi energy and D(E) DOSs at energy *E*. From Eqs. (11) and (12), the electronic specific heat $C_{V,\rm el}$ is given by

$$C_{V,\text{el}} = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} k_{\text{B}}^2 T D(\varepsilon_{\text{F}}) \equiv \gamma T.$$
(13)

The electronic specific heat coefficient, γ , is proportional to the DOSs at the Fermi level. In general, in pure metals, it is of the order of a few mJ/ mol K². Simply thinking, the electronic DOSs at the Fermi level is proportional to the effective mass of conduction electrons. The most conspicuous and noticeable systems with respect to their electronic specific heat coefficients are heavy electron systems that include some actinide and cerium compounds to be mentioned later. For example, in the case of a typical heavy electron system CeCu₆, the electronic specific heat coefficient reaches 1.5 J/mol K², which is more than 1000 times larger than that of a normal metal (Satoh et al., 1989).

The fundamental phenomena relevant for magnetic specific heat are the changes observed at the magnetic transition temperature and the excitations of magnons, which occur well below magnetic transition temperature. Quite often, the magnetic transitions are found to be secondorder phase transition phenomena. With temperature decreasing, when it reaches magnetic transition temperature, specific heat discontinuously increases. In reality, magnetic specific heat associated with second-order magnetic phase transitions is often of the so-called λ type, which is due to the influence of short-range magnetic order above the magnetic transition temperature. When magnetic transitions occur under pressure, specific heat is one of the effective measurements to follow the transition. Magnetic specific heat of a magnetically ordered material usually displays the $T^{3/2}$ temperature dependence in ferromagnetic compounds, and the T^3 temperature dependence is observed in antiferromagnetic compounds. In addition, it is well known that the temperature dependence of the specific heat is proportional to $T^3 \exp(\Delta_{mag}/k_{\rm B})$ when excitations of antiferromagnetic magnons have the energy gap Δ_{mag} . The proportionality coefficient

depends on exchange interaction. Thus one can clearly observe effects of pressure on exchange interactions and/or magnon excitations with energy gap.

Next, we consider the magnetic contribution to specific heat above magnetic transition temperature. In the paramagnetic state of the localized 4f electron system, the degeneracy of the energy levels can be removed by CEF. Specific heat $C_{\rm sch}$ in case of the two-level system with energy splitting Δ between the excited and ground states can be expressed as follows:

$$C_{\rm sch} = \frac{N\Delta^2}{k_{\rm B}T^2} \frac{g_0 e^{\Delta/k_{\rm B}T}}{g_1 [1 + (g_0/g_1) e^{\Delta/k_{\rm B}T}]^2}.$$
 (14)

This type of specific heat is called Schottky specific heat. Here, g_1 is degeneracy factor of the excited sate and g_0 is the degeneracy factor of the ground state. It results in a peak around 0.4 $\Delta/k_{\rm B}$ temperature region, having temperature dependency of T^{-2} at higher temperature and $T^{-2}\exp(-\Delta/k_{\rm B}T)$ at lower temperature. When symmetry varies with applied pressure, the change of the crystal field will also be reflected in specific heat measurement.

A special case is when electrical resistivity increases proportionally to $- \ln T$ with decreasing temperature in a dilute magnetic alloy, including magnetic impurities, such as a very small amount of manganese in copper. This phenomenon is called Kondo effect, and it is the most remarkable example of many-body effect in the metal. The magnetic moment of a d electron localized at a higher temperature is compensated by the spin of the conduction electron, and it is understood that the phenomenon appears via a process that involves forming a singlet ground state at low temperature. Usually, a peak in specific heat is observed around one-third of Kondo temperature T_K expressing the coupling strength between the localized magnetic moment and the conduction electron, and the total entropy of the Kondo effect is $R \ln 2$ (Kondo, 1968; Satoh et al., 1989; Yosida and Miwa, 1969; Yosida and Yamada, 1970).

One can observe the Kondo effect in intermetallic compounds including Ce, Yb, and U. In such compounds, values of the electronic specific heat coefficients 1000 times greater than that of normal metals are common. Thus, electrons in these compounds have extremely large effective mass as is understood from the following equation. Because of this, 4f electron Kondo systems are also called heavy electron systems. The localized magnetic moment of 4f electrons at a high temperature is coupled with the spin of the conduction electron below $T_{\rm K}$, thus becoming Fermi liquid (FL) having narrow bandwidth. As the total entropy is released from the ground state at T = 0 K to $T_{\rm F}$ is $R \ln 2$, γ value is considered to be

$$\gamma \approx \frac{R \ln 2}{T_{\rm F}} \tag{15}$$

 $T_{\rm F}$ is defined as the temperature when electrons condense into the FL state. If $T_{\rm F}$ decreases from about 10,000 K, Fermi energy in the normal metal, to the order of 10 K in the Kondo metal, γ will grow around 1000 times in value. The effect of pressure will be remarkable as we understand a heavy electron system, which has extremely narrow bandwidth.

Specific heat is also a powerful tool for characterizing superconducting properties of materials. In the case of an s wave superconductor, according to the BCS theory, superconducting specific heat can be described as follows:

$$C_{\rm s} \approx 1.34\gamma T_{\rm c} \left(\frac{\Delta(0)}{k_{\rm B}T}\right)^{3/2} \exp\left(-\frac{\Delta(0)}{k_{\rm B}T}\right),$$
 (16)

where $\Delta(0)$ is superconducting gap at T = 0. Thus, below the superconducting transition temperature, the electronic specific heat decreases as $\exp(-\Delta(0)/k_{\rm B}T)$, and one can determine $\Delta(0)$ from specific heat measurement performed below the superconducting transition temperature.

Recently, much attention has been paid to the so-called anisotropic gap state superconductor. At T = 0, $C_s(0)/\gamma T_c$ exhibits $(T/T_c)^3$ temperature dependence in the case of gap function with point node, while $(T/T_c)^2$ temperature dependence is observed in the case of gap function with line node. As low-energy excitation is possible, one can observe the power law T^n dependence at the low temperature in specific heat for p and d wave superconductors. The measurements of specific heat give extremely fruitful information about the superconducting gap complementary with other measurements, such as NMR. Even if a superconductor is not bulk, zero resistance may be observed when there is a continuous superconducting current path inside the sample. By using specific heat measurements, it is possible to determine whether superconducting behavior occurs in the bulk or not. We note that it is extremely important to check the bulk nature of pressure-induced SC by specific heat measurements under pressure.

3.1.2 Thermal expansion

It is well known that the length and/or volume of a material increases with increasing temperature. The fractional change $\Delta l/l$ of the length is called linear thermal expansion, and the coefficient of it, that is, the linear thermal expansion coefficient, α , is defined as the temperature derivative of the fractional change,

$$\alpha = \frac{1}{l} \frac{dL}{dT} = \frac{d}{dT} \left(\frac{\Delta l}{l} \right). \tag{17}$$

The volume thermal expansion coefficient α_V is defined in the same way:

$$\alpha_V = \frac{1}{V} \frac{\mathrm{d}V}{\mathrm{d}T}.$$
 (18)

The relation between α and α_V depends on the crystal structure of material. In the case of cubic system, these are connected by a very simple relation, $\alpha_V = 3\alpha$. Although the values of α show a parabolic dependence on the atomic number of the transition metal (number of *d*-electrons in the system) as shown in Figure 27A (White, 1979), the α and bulk modulus B_0 show a more complex behavior as functions of the atomic number for the rare earth elements as shown in Figure 27B (Benedict and Holzapfel, 1993;



FIGURE 27 (A) d electron number versus linear expansion coefficient α of transition metals (White, 1979). (B) Linear thermal expansion coefficient α (closed circles) and bulk modulus (solid line) B_0 of the rare earth elements (Benedict and Holzapfel, 1993; Spedding et al., 1961).

Spedding et al., 1961). It is well known that the volumes of lanthanides decrease with increasing atomic number (i.e., number of the 4f electrons), which is called "lanthanide contraction." Since the magnitudes of the α and B_0 are roughly inversely proportional to the lattice volume (White et al., 1984), the result in Figure 27B is well understood qualitatively from the lanthanide contraction except Eu and Yb.

Thermal expansion measurements provide a lot of information not only about the crystal structure but also about phase transformations (or crossover) in the electronic states. One of the characteristics of HF compounds is the anomaly in specific heat *C*, particularly the huge value of the electronic specific heat coefficient γ or large enhancement of *C*/*T* at low temperature. The specific heat at constant volume *C*_V is defined as

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial^2 F}{\partial T^2}\right)_V,\tag{19}$$

where *S* is the entropy and *F* is the Helmholtz free energy. On the other hand, the volumetric thermal expansion coefficient α_V is described by the following equation:

$$\alpha_V = \frac{1}{V} \frac{\partial V}{\partial T} = \frac{1}{B_T} \frac{\partial S}{\partial V} = \frac{1}{B_T} \frac{\partial^2 F}{\partial V \partial T},$$
(20)

where B_T is the isothermal bulk modulus defined as, $B_T = -V(\partial P/\partial V)_T = V(\partial^2 F/\partial V^2)_T$. These two equations imply that specific heat is the response of the entropy to the temperature and the thermal expansion coefficient is that to the volume or pressure. In other words, *C* and α describe the change of the entropy of a system in response to application of external forces such as temperature and pressure. This fact indicates a close relationship between *C* and α . *C* and α are related by the following equation, which is called "Grüneisen relation":

$$\alpha_V = \frac{\Gamma}{B_T V} C_V,\tag{21}$$

where Γ is dimensionless Grüneisen parameter. Γ is also defined as the volume dependence of a characteristic temperature T_{0} ,

$$\Gamma = \frac{\partial \ln T_0}{\partial \ln V}.$$
(22)

 T_0 may be considered as Kondo temperature $T_{\rm Kr}$ spin fluctuation temperature $T_{\rm sfr}$ and so forth. $\Gamma(T, V)$ relates the two strongly temperature-dependent quantities α_V and C_V but is relatively weakly dependent on temperature. Taking into account this fact and that for real solids Γ is often roughly constant over a wide range of temperatures, Γ has often been referred to as "the Grüneisen constant." But in some solids such as HF
compounds, it has been shown that Γ varies considerably with temperature since different contributions dominate the thermodynamic properties, especially at low temperatures (Visser et al., 1989; Thompson and Lawrence, 1994).

The temperature dependence of the thermal expansion coefficient α_V is usually represented at low temperature well below the Debye temperature Θ_D by the following equation (White and Collins, 1972):

$$\alpha_V(T) = A'T + BT^3, \tag{23}$$

where A' and B are the material characteristic constants. The first term may correspond to electronic and/or magnetic contribution and the second to the lattice contribution. The large value of A' indicates a large electronic and magnetic contribution. The above equation is derived easily using the well-known relation,

$$C_V(T) = \gamma T + \beta T^3, \tag{24}$$

where γ is the electronic specific heat coefficient and β is the lattice specific heat constant. The first term and the second term describe the contributions from electronic and phonon parts, respectively. Substituting Eq. (24) into Eq. (21), we obtain Eq. (23). Here, the coefficient A' is described as $A' = \gamma \Gamma / B_T V$ (Oomi et al., 1990b). If the values of Γ and B_T are weakly dependent on T, A' would be roughly proportional to γ , or to the DOSs at the Fermi level $D(\varepsilon_F)$. To determine whether the system is in an HF state or not, the value of C/T is usually plotted as a function of T^2 to examine whether there is a strong enhancement of this term at low temperature.

Rewriting Eq. (23) as follows:

$$\frac{\alpha_V}{T} = A' + BT^2,\tag{25}$$

one can also expect a large enhancement in the values of α_V/T as temperature decreases in HF systems. From the value of A', the information about $D(\varepsilon_{\rm F})$ and Γ is usually obtained, and then the electronic state of the system can be clarified. Further by measuring the thermal expansion coefficient, one can discuss the CEF and Kondo effect. This scenario is the same as that described in Section 3.1.1. Some experimental results will be shown in the following sections together with a brief discussion of the electronic state of HF compounds under high pressure.

3.2 Experimental measurements at high pressure

3.2.1 Specific heat

Figure 28 shows the schematic drawing of a miniature piston-cylinder pressure cell designed for the adiabatic method. The dimensions of the CuBe cylinder are 8.8 and 2.7 mm in outer and inner diameters,



FIGURE 28 Schematic of the miniature piston-cylinder pressure cell (Uwatoko et al., 2005).

respectively, and the cylinder is 21 mm long. ZrO₂ is used for the piston and the piston-backup. Gold-plated Cu is used for sample cell. Teflon may also be used for the sample cell, but its heat capacity exhibits strong pressure dependence, which increases the uncertainty of the background. The cell can be attached to a cryostat for specific heat measurement, and the same cell can be loaded into a Magnetic Property Measurement System (MPMS) in order to calibrate pressure at low temperature for the magnetization measurements, as also shown in Figure 28. For the measurements of specific heat, the thermometer and heater are fixed on the opposite swivels. These swivels are suspended from cold plate of ³He cryostat or mixing chamber of dilution refrigerator to an adiabatic space. The upper lock nut is installed on the upper swivel, and the lower swivel is fixed to the lower lock nut with a small screw as in Figure 28.

During the measurements of the heat capacity under pressure, changes in the heat capacity of the pressure media must be accounted for. For example, the change in the specific heat of Fluorinert 70/77 is large at low pressures, and it becomes smaller pressure increases. The data below 5 K have been fitted using the following equation: $C(P) = \gamma_{\text{glass}}(P)T + \beta(P)T^3$ because Fluorinert 70/77 becomes glass-like solid under pressure at low temperatures. These results and those fitted using

the asymptotic function f(P) = a/(P + b) + c in order to represent the specific heat of Fluorinert 70/77 at any pressure, where *a*, *b*, and *c* are the constants (Tomioka et al., 2008), show reasonable approximation of the heat capacity of this pressure-transmitting medium.

To avoid complications arising from the pressure variations of the background specific heat, it is possible to use solid AgCl as a pressuretransmitting medium. The pressure dependence of the specific heat of AgCl is negligibly small. However, liquid medium such as Fluorinert 70/77 is preferred for better hydrostaticity of the applied pressure.

To evaluate the performance of the described micro-pressure cell system in the temperature range from 0.7 to 5 K at pressure up to about 1.5 GPa, specific heat measurements of CeRhSi₃, which has a non-centrosymmetric tetragonal BaNiSn₃ structure, were carried out. This compound has a significantly enhanced electronic specific heat coefficient γ of about 120 mJ/mol K². Antiferromagnetic ordering temperature T_N has been reported to be 1.6 K and the magnetic entropy released is only 12% of R ln 2 below T_N (Muro et al., 1998). The SC appears above about 1 GPa where the antiferromagnetic transition vanishes (Kimura et al., 2005). Single crystal of CeRhSi₃, Fluorinert 70/77, and Pb with mass of about 37, 25, and 0.18 mg were loaded into the Cu sample cell. To maintain the hydrostaticity of pressure, the volume of CeRhSi₃ was about 40% of that of sample cell. The specific heat of CeRhSi₃ was measured at high pressure and will be described in detail in the following section. Figure 29 shows the temperature dependence of specific heat of the pressure cell, Fluorinert 70/77, and sample at ambient pressure. These are about 87%,



FIGURE 29 Temperature dependence of specific heat of the pressure cell, Fluorinert 70/77 and CeRhSi₃ sample at ambient pressure (Tomioka et al., 2008).

6%, and 7% of the total value at 2.5 K, respectively. One can see that the heat capacity of the pressure medium is a smooth function of temperature and a peak due to AFM transition is clearly observed at 1.6 K. Another conventional method to measure heat capacity under pressure, that is, temperature-modulated method (or AC method) can also be employed. This method has achieved a remarkable progress during the past decade (Sullivan and Seidel, 1968). Several laboratories have shown its applicability using majority of pressure generators, namely: piston cylinder (Tateiwa et al., 2005; Hashimoto et al., 2006), Bridgman anvils (Bouquet et al., 2000; Demuer et al., 2002), diamond anvils (Salce et al., 2000), and cubic anvils (Matsubayashi et al., 2010a).

3.2.2 Thermal expansion

The basic principle in experimental investigation in condensed matter physics is to detect a response of a physical quantity to an external force such as temperature (T), pressure (P), electric field (E), and/or magnetic field (H). In the high-pressure work until now, almost all of the measurements have been done with varying T, that is, changing only two of the external parameters (T, P). Developing a high-pressure apparatus suitable for high-pressure, high magnetic field, and low-temperature measurements should lead to highly quality data and result in better understanding of the electronic properties of condensed matter.

Here, we describe an apparatus which was designed to measure physical properties of condensed matter as function of *T*, *P*, and *H* (Honda et al., 2002; Oomi et al., 1993a). This apparatus is similar to that described by Swenson (1955) with some improvements, that is, taking the thermal expansion of the compression rod into account and possibility of use in high magnetic field. The ranges of *T*, *H*, and *P*, respectively, are $1.3 \le T \le 350$ K, $0 \le H \le 11$ T and $0 \le P \le 4$ GPa at hydrostatic condition.

Figure 30 shows a schematic cross-section of the high-pressure apparatus. Here, (1) is the pressure amplifier which generates loads up to 30 ton with an automatic control by a hydraulic pump; (2) is a piston made of SUS304; the He chamber is sealed by an O-ring; (3) the generated load is transmitted through the compression members; (4) and (5) to the high-pressure cell; (4) is an alternating pile of fiber-reinforced plastic (FRP) discs; and (5) is made from SUS304; in the present case, a piston-cylinder-type apparatus is shown, in which the tungsten carbide piston (8) and CuBe or NiCoCrMo(MP35N) alloy cylinders (9) are used; super-conducting magnet (10) is made of a NbTi superconducting coil located around (9); (6) is the thermal radiation shield; and (7) is a cryostat. The load is always kept constant automatically with less than $\pm 1\%$ error. (4) has a role not only as a compression member but also as a thermal insulator, which is a very important role when liquid He is used.



FIGURE 30 Schematic cross-section of the high-pressure apparatus. See the text for the details (Honda et al., 2002).

The maximum magnetic field is 9 T at 4.2 K (11 T at 2.2 K), and it is produced by an Oxford superconducting magnet, (10). The sample is placed inside the Teflon capsule, whose sample space is 4.5 mm in diameter and 20 mm in height. We usually employ a mixture of Fluorinert FC70 and FC77 or Daphne 7373 as the pressure-transmitting medium. The cylinder is made of MP35N alloy with HRC hardness of ~50 achieved after appropriate heat treatment. The outer and inner diameters are about 17.5 and 6 mm, respectively. The cylinder is tightened by insertion in a CuBe jacket with the thickness of 5 mm subjected to a force of about 10 ton, in order to increase the strength.

This high-pressure apparatus has been used for several different kinds of measurements such as electrical resistance, magnetic properties (magnetic susceptibility and magnetization), and thermal expansion (Honda et al., 2002). The thermal expansion at high pressure and high magnetic field measurements have been carried out by using strain gages and a conventional active-dummy method (Sakai et al., 1999).

3.3 Heat capacity at high pressure

The measurements of specific heat at high pressure have been done by many authors on different materials. Here, we describe a few typical examples: a HF compound CeAl₃; antiferrimagnetic compounds CeRhIn₅, CeIrSi₃, CeRhSi₃; a ferromagnetic compound UGe₂, which shows pressure-induced SC; and nonmagnetic narrow-gap semiconductor SmS.

3.3.1 CeAl₃

CeAl₃ is a typical HF compound which has $T_{\rm K}$ of 5 K and a large γ of 1620 mJ/mol K² at ambient pressure (Andres et al., 1975) as mentioned in Section 2.1.3.3. Figure 31 shows the specific heat of CeAl₃ as a function of temperature under pressure up to 0.82 GPa (Brodale et al., 1986). The broad maximum around 0.5 K suddenly disappears at 0.04 GPa. Recently, ferromagnetic correlations have been reported in this material (Andraka et al., 2009). The suppression of a broad heat capacity maximum is reasonably explained by proximity to QCP in the Doniach phase diagram (1977). The γ value decreases nonlinearly from 1200 at ambient pressure to 549 mJ/mol K² at 0.82 GPa. Brodale et al. suggested that C/T at 0.4 K has pressure dependence of $1.79 - 1.25P^{1/6}$. Since $T_{\rm K}$ is inversely proportional to γ value as described in Eq. (15), it is reasonable to consider that application of pressure leads to an increase of $T_{\rm K}$.



FIGURE 31 Pressure dependence of specific heat of CeAl₃ (Brodale et al., 1986).

3.3.2 CeRhIn₅

Knebel et al. (2004) studied pressure–temperature phase diagrams of the HF antiferromagnet CeRhIn₅ under hydrostatic pressure by ac calorimetry using diamond-anvil cell with argon as the pressure medium (Knebel et al., 2004). Figure 32 shows heat capacity of CeRhIn₅ at different pressures *P*. The data are normalized to T = 5 K. The inset shows specific heat previously measured at ambient pressure. The link between the collapse of the superconducting heat capacity anomaly and the broadening of the antiferromagnetic transition to an inhomogeneous appearance of SC below $P_c \approx 1.95$ GPa. Homogeneous bulk SC is only observed above this critical pressure. Knebel et al. discussed the influence of pressure inhomogeneities on specific heat anomalies, which emphasizes that the broadening of the transition near P_c is connected with the first-order nature of the transition.

3.3.3 CelrSi₃

Tateiwa et al. (2006) studied the pressure-induced superconductor CeIrSi₃ with the non-centrosymmetric tetragonal structure under high pressure by means of the electrical resistivity and ac heat capacity $C_{\rm ac}$ in the same run for the same sample as shown in Figure 33. The critical pressure was



FIGURE 32 Heat capacity of CeRhIn₅ at different pressures *P*. The data are normalized to T = 5 K. The inset shows specific heat measured at ambient pressure (Knebel et al., 2004).



FIGURE 33 Temperature dependences of C_{ac} of CeIrSi₃ (circles) and electrical resistivity (line) measured in the same experiment (Tateiwa et al., 2006).

determined to be $P_c = 2.25$ GPa, where the antiferromagnetic state disappears. The $C_{\rm ac}$ shows both antiferromagnetic and superconducting transitions at pressures close to P_c . On the other hand, the superconducting region is extended to high pressures of up to about 3.5 GPa, with the maximum transition temperature $T_{\rm sc} = 1.6$ K observed around 2.5–2.7 GPa. At 2.58 GPa, a large heat capacity anomaly was observed at $T_{\rm sc} = 1.59$ K. The jump of the heat capacity in the form of $C_{\rm ac}/C_{\rm ac}(T_{\rm sc})$ is 5.7 ± 0.1. This value is the largest one among previously reported superconductors, indicating the extreme strong-coupling SC. The electronic specific heat coefficient at $T_{\rm sc}$ is, however, approximately unchanged as a function of pressure, even at P_c (Tateiwa et al., 2006).

3.3.4 CeRhSi₃

Umehara et al., (2007) studied the pressure-induced superconductor CeRhSi₃ with the non-centrosymmetric tetragonal structure under high pressure by means of adiabatic specific heat and ac heat capacity. Figure 34 shows the temperature dependence of specific heat of CeRhSi₃



FIGURE 34 Temperature dependence of the specific heat of CeRhSi₃ at various pressures up to P = 1.22 GPa (Tomioka et al., 2008).

under various pressures up to P = 1.22 GPa in the temperature range from 0.7 to 2.5 K. At ambient pressure, a pronounced anomaly in the specific heat is observed, indicating the transition to an antiferromagnetically ordered state at $T_{\rm N} = 1.61$ K. $T_{\rm N}$ was defined as the temperature at which a peak appears in the C versus T plot. At 0.55, 0.78, 1.02, and 1.22 GPa, *T*_N are 1.81, 1.8, 1.58, and 1.44 K, respectively. Initially, *T*_N increases with increasing pressure and then decreases with increasing pressure up to 1.22 GPa. The specific heat jump at $T_{\rm N}$ is broadened with increasing pressure. And, a shoulder around 1.4 K can be seen for P = 0.55 GPa, and at the same temperature, a corresponding anomaly was found in the electrical resistivity data (Kimura et al., 2005). This anomaly may be a new magnetic transition. The magnetic contribution to the specific heat in CeRhSi₃ can be obtained by subtracting specific heat of nonmagnetic LaRhSi₃ from that of CeRhSi₃. LaRhSi₃ exhibits superconducting transition at $T_c = 2.4$ K at ambient pressure. Thus, the magnetic field B = 0.5 T was applied to LaRhSi3 in order to bring it to the normal state. The specific heat of LaRhSi₃ in the magnetic field B = 0.5 T shows the classical behavior $C = \gamma T + \beta T^3$ with $\gamma = 5.84$ mJ/mol K² and $\beta = 0.144$ mJ/mol K⁴.

In Figure 35, it can be seen that T_N lowers down to 1.2 K, and a minor discontinuity corresponding to SC appears around 0.8 K under pressure of 1.58 GPa (Tomioka et al., 2008). The magnetic entropy at T_N reaches 4.5% of *R* ln 2. It is remarkable that the discontinuity for the superconducting transition is very small in magnitude compared to what is observed in CeRhIn₅ (Section 3.3.2) and CeIrSi₃ (Section 3.3.3).



FIGURE 35 Specific heat of CeRhSi₃ at ambient pressure and at 1.58 GPa (Umehara et al., 2007).

Figure 36 shows the ac heat capacity of CeRhSi₃ at pressures ranging from 2.2 to 2.71 GPa. At 2.2 GPa, the heat capacity shows both antiferromagnetic and superconducting transitions. The superconducting transition is extremely weak at pressures close to P_c . However, the superconducting transition discontinuity becomes larger at 2.4–2.7 GPa, and the superconducting transition itself is observed at $T_{\rm sc} = 1.2$ K. At 2.71 GPa, the magnitude of the discontinuity in the heat capacity represented in the form of $\Delta C_{\rm ac}/C_{\rm ac}(T_{\rm sc})$ is about 4. This suggests that the strong-coupling SC appears in CeRhSi₃ as also observed in CeRhIn₅ (Section 3.3.2) and CeIrSi₃ (Section 3.3.3).

3.3.5 UGe₂

Figure 37A shows C/T of UGe₂ as a function of temperature at pressure of 1.13 GPa inside the pressure region where ferromagnetic phase is stable below ca. 1.8 GPa (see also Section 4). The anomaly associated with bulk superconducting transition is clearly observed at 0.7 K. The γ value rapidly increases around 1 GPa, which corresponds to the divergence of A value in the expression for AT^2 in the measurement of electrical resistivity as shown in Figure 37B. This strong enhancement of A and γ by applying pressure is in a reasonably good agreement with that calculated by a simple Stoner model and with ND measurements described in Section 2.2.2. This result strongly supports claims that decreasing of T_x is an important key in the mechanism of exotic SC of UGe₂. The details of physical properties in UGe₂ under high pressure will be further discussed in Section 4.



FIGURE 36 Temperature dependencies of the ac heat capacity of CeRhSi₃ at pressures between 2.4 and 2.7 GPa (Umehara et al., 2007).



FIGURE 37 (A) Temperature dependence of specific heat in the form of C/T at 0 and 1.13 GPa, and the ac susceptibility at 1.13 GPa in UGe₂. (B) Pressure dependence of A and γ values in UGe₂ (Tateiwa et al., 2001).



FIGURE 38 (A) Temperature dependence of specific heat under pressure for SmS. Inset shows $\ln C$ versus $\ln T$ plot. (B) Electronic specific heat C_e at selected pressures. Lines are fits using the Schottky model (Matsubayashi et al., 2007).

3.3.6 SmS

Black SmS is regarded as a nonmagnetic narrow-gap semiconductor crystallizing in the NaCl-type structure. It exhibits successive phase transitions with increasing pressure (Javaraman et al., 1970). An isostructural firstorder phase transition at low critical pressure P_{c1} (~0.7 GPa) at room temperature involves a valence change from divalent to mixed-valence state, accompanied by a spectacular color change from black to golden yellow. In the golden phase, it is assumed that the 4f⁶ level lies in the conduction bands, resulting in a mixed-valence state between 4f 6 and 4f 5 configurations (Varma, 1976). The magnetic susceptibility shows a weak temperature dependence similar to that of the prototypical mixed-valence compound SmB₆. Upon further increasing pressure above a high critical pressure $P_{c2} \sim 1.9$ GPa, the electrical resistivity switches to metallic behavior below a specific temperature $T_{\rm M}$ (Lapierre et al., 1981). Although broad studies during the past three decades revealed some aspects of SmS, it remains controversial whether there exists an energy gap at $E_{\rm F}$ in the golden phase (for $P_{c2} < P < P_{c2}$). Recent experimental development of specific heat

and thermal expansion measurements under pressure shed light on this problem and revealed that the pseudo gap state is formed below the critical pressure P_{c2} , above which a magnetically ordered state appears.

Figure 38 shows C of SmS under pressure. As the temperature is raised, C initially increases linearly with T (see the inset), indicating nonzero electronic specific heat γ . Then, a broad peak of heat capacity forms, which can be described by a conventional Schottky model with an energy gap Δ . The Schottky peak shifts to lower temperatures with increasing pressure, that is, Δ decreases with *P*. The presence of the energy gap is also observed in thermal expansion measurements under pressure. Figure 39 shows the T dependence of the linear thermal expansion coefficient α at pressures up to 2.16 GPa. In the "black phase" below P_{c1} , α is small and shows weak T dependence. When the system transforms into the golden phase, α_L suddenly changes and becomes strongly T dependent with a large negative peak. When pressure exceeds $P_{c2} \sim 1.9$ GPa, the Schottky anomaly disappears, and instead a sharp anomaly with a positive sign appears at $T_{\rm M} \sim 11$ K. As seen in Figure 40, the same anomaly was also detected by the ac specific heat measurements. Together with the observation of the internal field by nuclear forward scattering experiments (Barla et al., 2004), we ascribe the sharp anomaly to the phase transition between the paramagnetic and magnetically ordered states.

3.4 Thermal expansion at high pressure

In this section, we discuss thermal expansion coefficients of rare earth compounds that exhibit HF behavior, intermetallic compounds with magnetic order, and other compounds that exhibit valence fluctuations. In all of the examples, the temperature dependence of the thermal expansion is influenced significantly by applying pressure.

3.4.1 HF compounds

In this section, we introduce some examples of thermal expansion measurements of Ce-based HF compounds at ambient pressure and at high pressure. It is pointed out that there is a close relation between the thermal expansion coefficient and the heat capacity.

3.4.1.1 CelnCu₂ The cubic Heusler L21-type CelnCu₂ is HF compound with $\gamma = 1200 \text{ mJ/mol K}^2$ (Ōnuki et al., 1987). Figure 41 shows the values of $\Delta l/l$ of CelnCu₂ along the [100] direction as a function of *T* in the range, $4.2 \leq T \leq 300 \text{ K}$ (Oomi et al., 1990a). The large slope of $\Delta l/l$ versus *T* curve at low temperature shows a large value of thermal expansion coefficient α (CelnCu₂). To see this fact more clearly, we differentiate the $\Delta l/l$ with respect to *T*. The results are shown in Figure 42 for LalnCu₂ and the [100] direction of CelnCu₂. It is seen that α_{100} of CelnCu₂ is nearly the



FIGURE 39 Thermal expansion coefficient α of SmS as a function of temperature at selected pressures (Imura et al., 2008).



FIGURE 40 Typical specific heat curves of SmS shown as temperature variation of C_{ac}/T for several pressures. The data are normalized to 30 K (Haga et al., 2004).

same as that of LalnCu₂ above ca. 150 K, but the difference between them becomes very large as temperature decreases. α_{100} of CelnCu₂ is 9×10^{-6} K⁻¹ near 10 K, which is larger than that of LalnCu₂ by an order of magnitude.

In Figure 43, we plotted α/T as a function of T^2 for CelnCu₂ (α_{100}) and LaInCu₂. The value of α/T of CelnCu₂ is found to have a large increase



FIGURE 41 Temperature dependence of $\Delta l/l$ along [100] of single-crystalline CelnCu₂ and also for LaInCu₂ as a reference (Oomi et al., 1990a).



FIGURE 42 Thermal expansion coefficient α of CeInCu₂ and also for LaInCu₂ as functions of temperature (Oomi et al., 1990a).

with decreasing temperature below ca. 20 K. On the other hand, the α/T of LalnCu₂ is nearly independent of temperature. This behavior is in sharp contrast to that of CelnCu₂. The large enhancement in the magnitude of α/T was observed in other HF materials such as CeA1₃ (Kagayama et al., 1990), CeCu₆ (Oomi et al., 1990b), CeCu₂Si₂ (Takakura et al., 1990), and



FIGURE 43 Values of α/T as functions of T^2 for CelnCu₂ and LalnCu₂ (Oomi et al., 1990a).

 UPt_3 (Visser et al., 1985). These results show that it is one of the characteristic features of HF materials.

The behavior of α/T at low temperatures resembles large enhancement of C/T in HF materials. Taking into account the Grüneisen relation, which shows that α is roughly proportional to specific heat C, α is expected to have the same temperature dependence as C, that is, the present results seem to be consistent with this notion.

Since the α -*T* curve of LaInCu₂ is similar to that of normal metals (White and Collins, 1972), the approximation in which the α (LaInCu₂) originates mainly from phonon contribution may be reasonable. Here, we describe the observed α (CeInCu₂) as

$$\alpha(\text{CeInCu}_2) = \alpha_{\text{mag}} + \alpha_{\text{ph}} \cong \alpha_{\text{mag}} + \alpha(\text{LaInCu}_2), \quad (26)$$

where α_{mag} is the magnetic contribution to α due to 4f electrons. Then α_{mag} is approximated by the following equation:

$$\alpha_{\rm mag} \cong \alpha({\rm CeInCu}_2) - \alpha({\rm LaInCu}_2). \tag{27}$$

Figure 44 shows α_{mag} as a function of *T* for the [100] direction. α_{mag} increases with increasing temperature until it reaches a maximum around 25 K and then decreases with increasing temperature above 25 K. The origin of the maximum in Figure 44 is considered to arise from the CEF splitting of Ce³⁺ ion and then expected to behave as Schottky anomaly (Schefzyk et al., 1985).

Finally, we briefly discuss these results on the basis of our phenomenological theory (Oomi et al., 1988b). α_{mag} is shown to have the so-called Schottky-type temperature dependence if we assume a cubic symmetry



FIGURE 44 Magnetic contribution to the thermal expansion coefficient, $\alpha_{mag} = \alpha$ (CelnCu₂) - α (LaCuln₂), as a function of temperature (Oomi et al., 1990a).

and two levels with an energy difference Δ (K). α_{mag} has a maximum around 0.4Δ (= T_{max}). From the present data in which T_{max} is 25 K, Δ is estimated to be 63 K. This value is in good agreement with Δ = 65 K obtained by Ōnuki et al. (1987). The maximum in $\alpha_{mag'}$ (α_{mag})_{max'} is given by the following equation (Oomi et al., 1988b):

$$(\alpha_{\rm mag})_{\rm max} \approx 0.44 \frac{\kappa \eta k_{\rm B}}{3V_0},$$
 (28)

where κ is the compressibility, $k_{\rm B}$ is the Boltzmann constant, V_0 is the volume without CEF splitting, and η is $\partial \ln \Delta / \partial \ln V$. By substituting V_0 and κ for 7.8 × 10⁻²⁷ m³ and 0.9 × 10⁻² GPa⁻¹ = 0.9 × 10⁻¹¹ m³/J (Oomi et al., 1988a) and $(\alpha_{\rm mag})_{\rm max} \approx 7.6 \times 10^{-6} \text{ K}^{-1}$, we obtain $\eta = 30$. Thus, the result means that the value of Δ increases with pressure having a rate of 18 K GPa⁻¹, which is about five times larger than that of $T_{\rm K}$, $\partial T_{\rm K} / \partial P \approx 4$ K GPa⁻¹ (Kagayama et al., 1991a).

Figure 45 shows the temperature dependence of the linear thermal expansion coefficient α of CeInCu₂ below 80 K at various pressures (Kagayama et al., 1994d). At 0.3 GPa, α decreases smoothly with decreasing temperature but is still large around 10 K: it is about 300 times as large as that of Cu at 10 K. Such behavior is commonly observed in HF compounds. With increasing pressure α decreases, which implies that the DOSs decreases at high pressure as will be discussed later.

In Figure 46, the value of α/T is plotted as a function of T^2 at various pressures. α/T increases rapidly on cooling, like C/T, implying a large enhancement of $D(\varepsilon_F)$ or effective mass of electrons at low temperature.



FIGURE 45 The linear thermal expansion coefficient α of CelnCu₂ as a function of temperature at high pressure (Kagayama et al., 1994d).



FIGURE 46 The liner thermal expansion coefficient α of CelnCu₂ as a function of temperature at high pressure (Kagayama et al., 1994d).

By applying pressure, the value of α/T is suppressed: around 10 K, α/T at 2 GPa becomes about half of that at ambient pressure. The value of A' in Eq. (23) is generally dependent on temperature. In this review, it is assumed that α/T at a certain temperature is roughly proportional to the magnitude of A'. Figure 47 shows the pressure dependence of the value of α/T at 7 K. The ratio α/T decreases by applying pressure. In order



FIGURE 47 Pressure dependence of α/T of CelnCu₂ at 7 K (Kagayama et al., 1994d).

to derive the volume dependence of A', the Grüneisen parameter $\Gamma_{A'}$ for A' was estimated by fitting the data to the following equation:

$$A' = A_0' \left(\frac{V}{V_0}\right)^{-\Gamma_{A'}},$$
(29)

where A_0' and V_0 are the zero pressure values of A' and V, respectively. Using X-ray diffraction measurements at high pressure (Kagayama et al., 1990) to determine the relative change of volume V/V_0 in Eq. (29), $\Gamma_{A'}$ was calculated to be -34.

In a rough approximation that A' is inversely proportional to $T_{K'} - \Gamma_{A'}$ corresponds to the Grüneisen parameter of T_K , $\Gamma_K \equiv -\partial \ln T_K / \partial \ln V$ (see Eq. (3)). Kagayama et al. (1992a) mentioned that the Grüneisen parameter of T_K for CeInCu₂ is about 60, which was obtained by the volume dependence of the resistivity-maximum temperature or the coefficient of T^2 -dependent resistivity. The present value of 34 is of the same order of magnitude.

Finally, we comment about the pressure change in the overall behavior of α . Below 50 K, the α -*T* curve at 0.3 GPa has a negative curvature in contrast to those of normal metals (White and Collins, 1972). This behavior was also observed at ambient pressure but becomes less prominent at high pressure as is seen from Figure 45. The α -*T* curve of CeInCu₂ at 2 GPa seems to be similar to that of LaInCu₂. Such behavior at high pressure was observed also for CeNi compound (Okita et al., 1991) at high pressure as will be mentioned in Section 3.4.3. This fact implies that volume contraction shifts the system from the well-localized 4f (small T_K) state into the itinerant (large T_K) state: such pressure-induced crossover in the electronic state has been observed in several other Ce-based HF compounds. 3.4.1.2 **CeCu**₆ Next we consider CeCu₆, which is also a typical example of HF materials having the γ value of 1.7 J/mol K² (Satoh et al., 1989). The crystal structure is orthorhombic. Figure 48 shows the thermal expansion coefficients of single-crystalline CeCu₆ for each crystal axis. Large anisotropy in the α_t -*T* curves (i = a, b, and c) is seen in this figure. The temperature dependence of α_a is similar to that of a normal metal such as Cu or Ag. On the other hand, α_b shows anomalous temperature dependence: it increases rapidly with increasing temperature below 10 K, the rate of increase becomes small, showing a broad maximum around 80 K and then α_b decreases slowly above 100 K. The value of α_b at 10 K is about $10 \times 10^{-6} \text{ K}^{-1}$, which is larger than that of Cu ($0.03 \times 10^{-6} \text{ K}^{-1}$) by two orders of magnitude. α_c also shows anomalous temperature dependence: α_c decreases with decreasing temperature, having the same temperature



FIGURE 48 Temperature dependencies of linear thermal expansion coefficients, $\alpha_i = (1/l_i)(dl_i/dT)$, of single-crystalline CeCu₆ (circles) and La (triangles), where *i* denotes *a*, *b*, and *c* (Oomi et al., 1990c).

dependence as that of LaCu₆ until it becomes zero around 30 K, and then it begins to increases upon further cooling to the value of about 7×10^{-6} K⁻¹ near 5 K. Such increase was also found in the thermal expansion coefficient of single-crystalline UPt₃ (Visser et al., 1985).

Results obtained for CeCu₆ are similar to those for CeInCu₂, where a large enhancement in the magnitude of A', that is, in the electronic and magnetic contributions was observed (Oomi et al., 1990b). The large enhancement in the magnitude of α/T is also observed in other HF materials including U-compounds. Considering the fact that there are no such effects in the normal metals and alloys, the anomalously large enhancement of α/T is one of the characteristics of Ce- and U-based HF materials. Further, as was already noted, the anomalous behavior of the thermal expansion coefficient is closely related to the anomalous behavior of heat capacity *C* by the Grüneisen relation, Eq. (21). In Table 3, we

Compound	α/T (10 ⁻⁹ K ⁻²) (at 10 K)	Reference	C∕T (mJ∕ mol K²) (at 10 K)	Reference
CeAl ₃	600	Kagayama et al. (1990)	350	Flouquet et al. (1982)
CeCu ₆	430	Oomi et al. (1990c)	360	Kato et al. (1987)
CeCu ₂ Si ₂	360	Takakura et al. (1990)	140	Stewart (1984)
CeInCu ₂	1000	Oomi et al. (1989)	340	Ōnuki et al. (1987)
CeCu ₂	30	Uwatoko et al. (1990)	180	Ōnuki et al. (1985b)
CeRu ₂ Si ₂	170	Lacerda et al. (1989)	220	Fisher et al. (1988)
YCu ₂	10	Uwatoko et al. (1990)	50	Luong et al. (1985)
LaCu ₆	5	Oomi et al. (1990c)	120	Kato et al. (1987)
LaAl ₃	10	Kagayama et al. (1990)	21	Edelstein et al. (1987)
LaCu ₂ Si ₂	40	Takakura et al. (1990)	33	Takeda et al. (2008)
LaInCu ₂	240	Oomi et al. (1989)	166	Sato et al. (1992)

TABLE 3 Relation between the values of α/T and C/T at 10 K for HF compounds and reference materials (Y and La compounds)

summarized the data of C/T and α/T . It is found that there is a close relation between C/T and α/T of HF compounds. In conclusion, we emphasize that large enhancement of α/T (or α_V/T) at low temperature should be one of the most important characteristics of HF materials.

Next we will consider the effect of pressure on the anisotropic properties in the thermal expansion coefficients of single-crystalline CeCu₆. Figure 49 shows α_a at ambient and 0.82 GPa. No significant difference in the α_a is found within experimental errors between ambient and 0.82 GPa. In Section 2, the linear compressibility along *a*-axis, κ_a , is very small compared to κ_b and κ_c (Shibata et al., 1986). This fact indicates that the binding force along the *a*-axis is the largest among the three axes. The length of the *a*-axis is not affected much by the magnetic field (Oomi et al., 1988a). From these facts, the *a*-axis is not significantly affected by applying external forces.

 α_b –*T* curves of CeCu₆ are shown in Figure 50 at ambient pressure, 0.76 and 1.26 GPa. The value of α_b is found to be affected significantly by applying pressure: α_b at 50 K is 12×10^{-6} K⁻¹ at ambient pressure and 8.0×10^{-6} K⁻¹ at 1.26 GPa. This result is in sharp contrast with that of α_a . In the foregoing paragraph, it was mentioned that there is a large magnetic contribution to the magnitude of α_b , which is due to the existence of unstable 4f electrons. Thus the large effect of pressure on the magnitude of α_b is caused by the instability of 4f electronic states in CeCu₆.

Temperature dependence of α_c of CeCu₆ below 50 K is shown in Figure 51 at ambient pressure, 0.32, 0.63, and 1.26 GPa. The overall behavior of α_c –*T* curve at high pressure is almost similar to that at ambient pressure. The temperature showing the minimum in α_c , T_{min} , is almost independent of pressure. But the value of $\alpha_c(T_{min})$ is found to increase with increasing pressure from a small negative value to a positive one at



FIGURE 49 Temperature dependence of α_a of CeCu₆ at ambient pressure and at 0.82 GPa (Oomi et al., 1991).



FIGURE 50 Temperature dependence of α_b of CeCu₆ at ambient and high pressures (Oomi et al., 1991).



FIGURE 51 Temperature dependence of α_c of CeCu₆ at high pressure (Oomi et al., 1991).

0.63 GPa. Since α_c curve at 0.63 GPa is the same as that at 1.26 GPa, $\alpha_c(T_{\min})$ is independent of pressure above 0.63 GPa. The origin of this behavior is not clear.

It should be noted that the maximum in the ρ -*T* curve, ρ_{max} , of CeCu₆ decreases with increasing pressure, but above 1 GPa, ρ_{max} becomes nearly constant (Thompson and Fisk, 1985). This was explained by assuming that the valence of Ce atom changes significantly at low pressure but the change becomes small at high pressure. Thermal expansion results may be interpreted on the basis of the same assumption. Further, it is interesting to note that $\alpha_c(T_{min})$ changes significantly below 1 GPa, but it shows saturation above 1 GPa, which is the same behavior as that of ρ_{max} . This fact suggests that the pressure. In the foregoing section, it was reported a large enhancement of the value of α/T at low temperature, which is

originated from the enhancement of the effective mass of conduction electrons. As mentioned above, the change in the magnitude of α by applying pressure is dominated by a decrease in the value of α_b , which decreases considerably at high pressure. Considering this fact, it is expected that the enhancement of α_1/T at low temperature is suppressed by applying pressure. This means that the effective mass of electrons decreases at high pressure. This conclusion is consistent with the results obtained by heat capacity measurement at high pressure as mentioned in Section 3.3.1.

3.4.2 Kondo compounds with magnetic order

There are numerous materials showing Kondo effect accompanied by magnetic order, antiferrromagnetism or ferromagnetism. In this section, we show the experimental results for antiferromagnetic materials, CeRh₂Si₂ ($T_N = 36$ K), CeAu₂Si₂ ($T_N = 8$ K), and ferromagnetic material, $GdAl_2$ ($T_C = 162$ K). Since the electrical resistance and other physical properties of these compounds will be mentioned in detail in Section 4, we will confine our discussion here to thermal properties. It is well known that in these compounds, the Kondo effect competes with the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions, which induce magnetic ordering. A variety of magnetic properties of rare earth compounds have been explained on the basis of the interplay of these interactions. Doniach presented a theoretical phase diagram by taking into account these facts to explain the electronic and magnetic states of rare earth compounds which is the so-called Doniach's phase diagram. The rough schematic of this diagram is depicted in Figure 52. In the diagram, the characteristic temperatures such as $T_{N_{\ell}}$, $T_{K_{\ell}}$ and T_{RKKY} are shown as a function of J/W, where J is the exchange coupling strength, and bandwidth W is nearly proportional to $1/D(\varepsilon_{\rm F})$. The magnitude of I/W is



FIGURE 52 Doniach phase diagram after Brandt and Moshchalkov (1984).

proportional to pressure. The $T_{\rm M}$ has a peak at a value of J/W, where $T_{\rm K} = T_{\rm RKKY}$. At present, CeRh₂Si₂ is considered to be on the right hand side of the peak, but CeAu₂Si₂ is on the left hand side.

3.4.2.1 *CeRh*₂*Si*₂ CeRh₂*Si*₂ crystallizes in the ThCr₂*Si*₂ tetragonal structure and shows two kinds of antiferromagnetic orderings at 36 K (= T_{N1}) and 24 K (= T_{N2}) (Kawarazaki et al., 2000). More details about this compound will be mentioned in Section 4.2.1. It has been reported that T_{N1} disappears at a relatively low pressure around 1 GPa, in spite of such high T_N (Settai et al., 1997). The resistivity anomaly at T_{N1} becomes broader by applying high pressure, and no anomaly is observed at T_{N2} . The exact value of the critical pressure P_c , where the AFM disappears, is difficult to identify from earlier electrical measurements (Ohashi et al., 2002). Each magnetic transition has been reported to be accompanied by pronounced thermal expansion anomalies.

Figure 53 (Honda et al., 1999) shows the fractional change in length $\Delta l/l$ as a function of temperature *T* below 300 K. As temperature increases, the value of $\Delta l/l$ decreases gradually followed by two steps near 25 K (= T_{N2}) and 37 K (= T_{N1}) due to magnetic phase transitions and then begins to increase smoothly above 38 K. A clear spontaneous MS is observed below T_{N1} having an order of magnitude of 10^{-4} .

Figure 54 shows the temperature evolution of $\Delta l/l$ in the range from 10 to 50 K at high pressure below 2.15 GPa. Two distinct anomalies due to magnetic transition are seen in the temperature dependence of $\Delta l/l$ at ambient pressure as mentioned above. Below 1.1 GPa ($\sim P_c$), the spontaneous MS is clearly observed. Since both the MS effect and the thermal



FIGURE 53 Linear thermal expansion of $CeRh_2Si_2$ at ambient pressure (Honda et al., 1999).



FIGURE 54 Linear thermal expansion of CeRh₂Si₂ at low temperature at various pressures. The arrows indicate the magnetic phase transition temperatures, T_{N1} and T_{N2} (Honda et al., 1999).

expansion anomalies are not detected above 1.1 GPa, that is, the thermal expansion $\Delta l/l$ (and also the thermal expansion coefficients) increases smoothly with temperature. The critical pressure P_c where the AFM disappears is assumed to be around 1.1 GPa. It is seen that the magnetic phase transition temperatures, T_{N1} and T_{N2} indicated by the arrows in Figure 54, decrease with increasing pressure.

An example of α -*T* curves is shown at various pressures in Figure 55 below 50 K. Significant changes in α are easily seen as pressure increases. Two anomalies are found at ambient pressure at $T_{\rm N1} = 37$ K and $T_{\rm N2} = 26$ K, but at 1.06 GPa, one broad minimum in the α -*T* curve is observed around 15 K, that is, $T_{\rm N2}$ disappears above this pressure. Above 1.09 GPa, no anomalies are found in the behavior of the thermal expansion coefficient. In other words, the AFM is suppressed completely above 1.09 GPa. $T_{\rm N1}$ and $T_{\rm N2}$ are found to decrease rapidly with increasing pressure and extrapolated to be 0 around 1.11 GPa (= $P_{\rm c1}$) and 0.55 GPa (= $P_{\rm c2}$), respectively. The pressure dependence of $T_{\rm N1}$ and $T_{\rm N2}$ will be summarized in Figure 57. At high pressure around 1.06 GPa, α shows a



FIGURE 55 Thermal expansion coefficients α of CeRh₂Si₂ at high pressure (Oomi and Kagayama, 2006).

broad maximum around 30 K, which may be due to the CEF splitting of the sixfold degenerate 4f levels of Ce^{3+} ion. Since the maximum is suppressed with increasing pressure, the present result indicates that the effect of CEF splitting disappears at high pressure. In other words, the 4f electron of Ce is delocalized at high pressure. The magnetic properties of Ce compounds at high pressure are generally explained using the Doniach phase diagram assuming that $JD(\varepsilon_F)$ is proportional to pressure *P*.

For CeRh₂Si₂, the RKKY interactions overcome the Kondo interactions at ambient pressure because the ground state is antiferromagnetic. When pressure increases, the Kondo interactions increase more rapidly than the RKKY interactions. This means that the localized 4f moment disappears at a critical pressure P_c (=1.1 GPa) inducing a Kondo spin compensated state that has large critical fluctuations. Just above $P_{c'}$ we expect a large contribution of spin fluctuations to physical quantities, which manifests itself as large values of α and of the coefficient of the T^2 term in the electrical resistivity. The value of α around 10 K is 2–3 × 10⁻⁶ K⁻¹ at 1.11 GPa, which is much larger than that of normal metals such as Cu, $\alpha(10 \text{ K}) = 0.03 \times 10^{-6} \text{ K}^{-1}$. Considering that T_N decreases with pressure, CeRh₂Si₂ should be placed on the right hand side of the peak of the phase diagram and then the Kondo state is stabilized above a critical value of *J* or P_c .

In order to examine the pressure dependence of α , the values are shown as a function of pressure in Figure 56. At 10 K, α shows a discontinuous change around 1.1 GPa, which corresponds to the disappearance of antiferromagnetic order or QCP. At 30 K, thermal expansion coefficient also shows an anomaly near 1 GPa, in which the change in the magnitude of α seems to be larger than that at 10 K. It is quite surprising that there are discontinuous changes near 1 GPa in α curves at both 50 and 60 K, which are higher than the magnetic transition temperature of 35 K. This fact indicates that there are anomalies in the pressure dependence in α near 1 GPa even in the paramagnetic region.

This result is similar to the case of UGe₂, which is a typical example of pressure-induced SC (Saxena et al., 2000). For this material, Oomi et al. (2003) reported the anomalous pressure dependence in the thermal expansion coefficients and electrical resistance in the temperature range above the ferromagnetic ordering temperature. In this case, the existence of some kinds of short-range order having crystalline or magnetic origins was suggested. According to this consideration, it appears that there may be disorder or magnetic short-range order in CeRh₂Si₂ specimen in the region above T_N , which gives rise to an anomaly in the pressure dependence of α . In such sense, the large pressure effect on the magnitude of α at



FIGURE 56 Thermal expansion coefficients α of CeRh₂Si₂ as a function of pressure at various temperatures (Oomi and Kagayama, 2006).

30 K above 1.1 GPa may be due to a large quantum fluctuations effects, which may exist in the wide range of P-T phase diagram (see, e.g., Sachdev, 1999a,b).

Figure 57 (Oomi and Kagayama, 2006) summarizes the present status of pressure data of CeRh₂Si₂ including superconducting phase. Some discrepancies exist about the pressure range of SC (Araki et al., 2003; Movshovich et al., 1996). But it should be emphasized that there is another phase boundary (dotted line in Figure 57) in the paramagnetic region, which is extrapolated to the maximum of the $T_{\rm C}$ versus *P* curves. This is also similar to the *P*–*T* phase diagram of UGe₂ (Oomi et al., 2002; Saxena et al., 2000). This result means that there is a phase boundary or crossover which is closely related to the occurrence of SC. In the region $T > T_{\rm N1}$ and $P > P_{\rm cr}$ precursor phenomena for the pressure-induced SC may be observed. This fact may give a hint in exploring the pressure-induced SC in condensed matter. The details of the transport properties of CeRh₂Si₂ and UGe₂ will be described in the following section.

3.4.2.2 *CeAu*₂*Si*₂ Here, we show the pressure dependence of thermal expansion of $CeAu_2S_2$ which also crystallizes in the tetragonal $ThCr_2Si_2$ structure. This compound shows an AFM order below 8 K, which is accompanied by a hump-type anomaly and a peak in resistivity and



FIGURE 57 P-T phase diagram of CeRh₂Si₂ (Oomi and Kagayama, 2006). T_c was obtained from Movshovich et al. (1996) and Araki et al. (2003).

magnetic susceptibility, respectively, as shown in Figure 58 (Sakai, 2009). Here, we focus on this type of AFM in CeAu₂Si₂, even though it has been reported that several different types of magnetic order may exist depending on the slight variation of sample composition (Fujiwara et al., 2006; Honda et al., 2004).

Linear thermal expansion $\Delta l/l_a$ and $\Delta l/l_c$ along *a*- and *c*-axes of CeAu₂Si₂ around T_N are displayed in Figure 59. They are almost independent of temperature immediately above T_N (~8 K). $\Delta l/l_a$ changes slope at T_N , and a negative thermal expansion coefficient $\alpha < 0$ is observed below T_N . On the other hand, $\Delta l/l_c$ shows opposite downward change of slope at T_N and a positive value of α below T_N . We define the crosspoint between the two extrapolated lines just above and below the slope



FIGURE 58 Temperature dependence of (A) resistivity and (B) magnetic susceptibility of CeAu₂Si₂ (Sakai, 2009).



FIGURE 59 Temperature dependence of linear thermal expansion along tetragonal a-and c-axes of CeAu₂Si₂ (Sakai, 2009).

breaking points as T_N and estimated them to be 7.4 and 7.6 K for the *a*- and *c*-axes at ambient pressure, respectively.

The temperature dependences of $\Delta l/l_a$ and $\Delta l/l_c$ at various pressures are shown in Figure 60. The upward behavior of $\Delta l/l_a$ becomes clearer, while the downward one is suppressed as pressure increases. As shown in Figure 61, T_N evaluated from both $\Delta l/l_a$ and $\Delta l/l_c$ increases with increasing pressure, shows a broad maximum around 1.5 GPa (= P_{max}), and then decreases. These results are consistent with those obtained by electrical resistivity measurements while those obtained from magnetic susceptibility data show monotonous decease with increasing pressure (Sakai, 2009). Pressure derivative of T_N , dT_N/dP , above P_{max} is evaluated to be -0.34 and -0.26 for $\Delta l/l_a$ and $\Delta l/l_c$, respectively, predicting that the QCP exists above 20 GPa. These values are roughly consistent with those evaluated from the experimental result of the resistivity, susceptibility, and the previous report (Garde and Ray, 1994).

To investigate the pressure dependence of T_N up to 2.5 GPa, the data discussed here were analyzed using standard thermodynamics relationships. The pressure coefficient of T_N was evaluated by using the Ehrenfest's relation

$$\frac{\mathrm{d}T_{\mathrm{N}}}{\mathrm{d}P} = T_{\mathrm{N}}\varDelta\left(\frac{\partial V}{\partial T}\right)\frac{1}{\varDelta C_{P}},\tag{30}$$

where ΔC_P is the specific heat jump at T_N . The temperature derivative of volume between just below and above T_N is calculated from the following equation:



FIGURE 60 Pressure dependence of linear thermal expansion along tetragonal a- and c-axes of CeAu₂Si₂ (Sakai, 2009).

$$\frac{\partial V}{\partial T} = V \left(2 \frac{\partial}{\partial T} \frac{\Delta a}{a} + \frac{\partial}{\partial T} \frac{\Delta c}{c} \right), \tag{31}$$

using a $\Delta C_P = 2 \text{ J/mol K}$ (Fujiwara et al., 2006) and a = 4.32, c = 10.19 Å. From this equation, dT_N/dP was estimated to be $+0.5 \text{ K GPa}^{-1}$ which is consistent with that obtained from thermal expansion measurement up to 1 GPa. Here, positive value of $\Delta(\partial V/\partial T)$ indicates positive dT_N/dP because signs of a T_N and ΔC_P are always positive for finite T_N independent of pressure. Inset of Figure 61 displays $\Delta(\partial V/\partial T)$ as a function of pressure. $\Delta(\partial V/\partial T)$ decreases with increasing pressure and becomes negative above 1.2 GPa, indicating that T_N increases up to 1.2 GPa and decreases above 1.2 GPa. This is consistent with the experimental result as shown in Figure 61.

3.4.2.3 *GdAl*² Next, we consider the ferromagnetic compound GdAl² having cubic C15-type structure. The Curie temperature $T_{\rm C}$ of GdAl² is 168 K, which is the highest among RAl² (R = rare earth element) ferromagnetic compounds (Purwins and Leson, 1990). Previous reports have revealed that spontaneous magnetic moment is between 6.83 and 7.20 $\mu_{\rm B}$



FIGURE 61 T_N evaluated from thermal expansion along *a*- and *c*-axes of CeAu₂Si₂ as a function of pressure. Inset: $\Delta(\partial V / \partial T)$ calculated using Eqs. (30) and (31). The solid and broken curves are the guides to the eye for *a*- and *c*-axes, respectively (Sakai, 2009).

per Gd atom (Lee and Montenegro, 1981). The elastic properties are also anomalous because the longitudinal elastic constant C_L increases below T_c , that is, the lattice becomes hard in response to the magnetic ordering (Schiltz and Smith, 1974). This is in sharp contrast with the elastic properties of other ferromagnetic materials such as Invar alloys (Oomi et al., 1981b). Since the magnetic and elastic properties of GdAl₂ are anomalous, it is interesting to study the relationship between magnetism and volume of GdAl₂ not only at ambient pressure but also at high pressure.

Figure 62 shows the temperature dependence of the linear thermal expansion $\Delta l/l$ at various pressures. $\Delta l/l$ decreases almost linearly with decreasing temperature. But the decrease below $T_{\rm C}$ becomes steeper than that above $T_{\rm C}$. This fact indicates that the magnitude of the thermal expansion coefficient below $T_{\rm C}$ is larger than that above $T_{\rm C}$. In other words, the compound exhibits a negative MS, that is, the length (or volume) shrinks as the result of magnetic ordering. By applying pressure, the decrease in $\Delta l/l$ is found to be less prominent.

The linear thermal expansion expansion coefficient α was obtained from the result depicted in Figure 62 by differentiating $\Delta l/l$ with respect to *T*. An example of the result at ambient pressure and 2 GPa is shown in Figure 63 as a function of temperature. *T*_C was determined as the



FIGURE 62 Thermal expansion of GdAl₂ at high pressure (Fuchizaki et al., 2006).



FIGURE 63 Thermal expansion coefficient of $GdAl_2$ at ambient pressure and at 2.0 GPa (Fuchizaki et al., 2006).

temperature where α curve begins to increase suddenly with decreasing temperature (see the two lines in Figure 63). $T_{\rm C}$ at ambient pressure is 168 K. The magnitude of the discontinuous change in α below $T_{\rm C}$ decreases with increasing pressure. The pressure dependence of $T_{\rm C}$ is shown in Figure 64. $T_{\rm C}$ is found to increase with pressure almost linearly below 2 GPa at the rate $\partial T_{\rm C}/\partial P = 8.56$ K GPa⁻¹, which is slightly higher than 7.1 K GPa⁻¹, as reported previously (Jaakkola, 1994). The magnitude of $\partial T_{\rm C}/\partial P$ may be estimated by using the Ehrenfest relation to be 10 K GPa⁻¹. Considering the ambiguities of the estimation and a



FIGURE 64 T_c of GdAl₂ as a function of pressure (Fuchizaki et al., 2006).

difference in the samples used in the two studies, this result is in good agreement with the earlier results.

To extract the spontaneous volume MS ω , we approximate the volume thermal expansion $\omega(T) (=\Delta V/V = 3\Delta l/l)$ into two contributions: one is from the phonon (lattice vibration) $\omega_{\rm ph}$ and the other one is from the spontaneous volume MS $\omega_{\rm s}$:

$$\omega = \omega_{\rm ph} + \omega_{\rm s}. \tag{32}$$

The magnitude of $\omega_{\rm ph}$ was calculated on the basis of the Debye model and the Grüneisen relation (Oomi and Môri, 1981b). Figure 65 illustrates the values of ω at ambient pressure, in which the broken line shows the result of fitting. The $\omega_{\rm s}$ at ambient pressure was estimated to be about -1.5×10^{-3} at 0 K, which is negative and is smaller than that of Invar alloy by an order of magnitude.

Figure 66 shows $-\omega_s$ at high pressure. The magnitude of ω_s (at 77.4 K) is shown in the inset of Figure 66: it decreases rapidly below 1 GPa and tends to saturate above that.

Figure 67 shows the relative volume V/V_0 as a function of pressure up to 12.4 GPa at room temperature, where V and V_0 are the volumes at high and ambient pressures, respectively. The volume shows a smooth decrease with increasing pressure without any discontinuities. This fact indicates that there is no structural phase transition, that is, the C15 structure is stable up to 12.4 GPa at room temperature. The bulk modulus was estimated by using first-order Murnaghan's equation of state (see Eq. (1) in Section 2). The solid curve in Figure 67 shows the result of least-square fitting, and we obtained the bulk modulus to be 75.3 GPa.



FIGURE 65 Fractional volume change ω of GdAl₂ at ambient pressure (Fuchizaki et al., 2006).



FIGURE 66 Temperature dependence of the spontaneous volume magnetostriction ω_s of GdAl₂ at high pressure. The inset shows ω_s at 77.4 K at high pressure (Fuchizaki et al., 2006).

In order to examine the volume dependence of T_{C} , the above data will be discussed using Grüneisen parameter Γ . Grüneisen parameter for T_{C} is defined as follows:

$$\Gamma = -\frac{\partial \ln T_{\rm C}}{\partial \ln V} = \frac{B_0}{T_{\rm C}} \left(\frac{\partial T_{\rm C}}{\partial P}\right). \tag{33}$$


FIGURE 67 Relative volume change of $GdAl_2$ as a function of pressure at room temperature (Fuchizaki et al., 2006).

Using the data obtained above, we estimated Γ as 3.84, which is larger than that of Ni (Γ = 1) but nearly the same as that of TbAl₂ (Γ = 3.8). Grüneisen parameter of Kondo temperature of HF materials is usually of the order of 100 (see Section 4). This fact suggests that the ferromagnetism of GdAl₂ is stable under the influence of external force.

3.4.3 Valence fluctuating compound CeNi

CeNi is a typical valence fluctuating compound having the Kondo temperature of about 100–150 K. The compound has the orthorhombic CrB type crystal structure with the lattice constants, a = 3.784 Å, b = 10.564 Å, and c = 4.363 Å. The low symmetry leads to a large anisotropy in the physical properties such as magnetic properties and thermal expansion. The valence fluctuating state is originated from the strong hybridization between the conduction band and 4f electrons. Since the hybridization depends strongly on the external forces, the valence fluctuating state may be significantly affected by high pressure. The lattice properties of CeNi under high pressure were studied by Okita et al. (1991) and Uwatoko et al. (1993) by using strain gage method.

The lattice compression is highly anisotropic, in which the *c*-axis is the hardest among the three axes. The linear compressibilities are in the order, $\kappa_b > \kappa_a > \kappa_c$. Figure 68 shows the temperature dependence of the linear thermal expansion coefficients along the three crystal axes, α_i (i = a, b, and c) at ambient pressure. The α_i curves are found to be largely different among each crystal axis. The values of α_a and α_c are positive and have a maximum around 105 and 75 K with values of 200 and 73 × 10⁻⁶ K⁻¹, respectively. On the other hand, α_b is negative below



FIGURE 68 Temperature dependence of the linear thermal expansion coefficients of CeNi single crystal, $\alpha_i = (l/l_i) (dl_i/dT)$, where i = a, b, or c (Uwatoko et al., 1993).



FIGURE 69 Volume thermal expansion coefficients of CeNi and LaNi defined as $\alpha_V = (\alpha_a + \alpha_b + \alpha_c)/3$ (Uwatoko et al., 1993).

170 K and has a minimum around 106 K with the value of -53×10^{-6} K⁻¹. The overall behavior at ambient pressure is approximately the same as that reported previously (Gignoux et al., 1983). Here, the value of α_V was defined as $(\alpha_a + \alpha_b + \alpha_c)/3$ to compare the linear thermal expansion coefficient. As is seen from the results in Figure 68, the magnitudes of α_i of CeNi are extremely large compared with those of normal metals: α_c is 200×10^{-6} K⁻¹ around 100 K, which is two orders of magnitude larger than that of a normal metal. The large value of α_i may be related to unstable electronic states of CeNi. Figure 69 shows the α_V for

CeNi and LaNi as a function of temperature at ambient pressure. LaNi was used as a reference material because La has no 4f electrons. α_V is found to have a maximum at 92 K with a value of 70×10^{-6} K⁻¹. The temperature dependence of α_c is similar to that of $\alpha_{V'}$ in which the contribution of CEF splitting may be the origin of the maximum. It should be noted that the magnitude of $\alpha_{V'}$ is larger than that of normal metals over a wide temperature range. This reflects the fact that bulk modulus of CeNi (~26 GPa at room temperature) is also extremely small. The $\alpha_{V'}$ of LaNi increases smoothly with temperature like in normal metals.

Thermal expansion coefficient α_c of CeNi at various pressures is shown in Figure 70 as a function of temperature. At ambient pressure, α_c increases rapidly with increasing temperature, followed by a maximum near 75 K. This Shottky-type peak is due to CEF splitting of the sixfold degenerate 4f level of Ce³⁺ ions (Uwatoko et al., 1993). The value of $\alpha_c(\max)$ is found to decrease with increasing pressure: α_c of CeNi at 1.37 GPa is almost to the same as that of LaNi and the maximum in α_c seems to disappear above 1 GPa below room temperature. The temperature showing the maximum in the α_c -*T* curve increases rapidly with increasing pressure with the rate of the order of 100 K GPa⁻¹ and the peak is smeared out. Since α_c of CeNi at 1.37 GPa is almost identical to that of nonmagnetic LaNi, the effect of CEF splitting may disappear at high pressure above 1 GPa.

Here, we analyze the data according to Eq. (23). Assuming that α_c of CeNi is roughly the same as that of α_V , the values of A' are obtained as a function of pressure. Figure 71 shows the result. It is found that the value of A' decreases smoothly with pressure. The value of A' at ambient pressure is very large compared with other HF compounds (Uwatoko et al., 1993). Since the magnitude of A' is roughly proportional to the DOSs at the Fermi level $D(\varepsilon_F)$ and Grüneisen parameter, the present results indicate high DOSs at



FIGURE 70 Thermal expansion coefficient α_c of CeNi single crystal under hydrostatic pressure. The maximum in α_c is shown by an arrow (Uwatoko et al., 1993).



FIGURE 71 The values of A' for CeNi as a function of pressure (Uwatoko et al., 1993).

the Fermi level, large Grüneisen parameter, and low bulk modulus. The decreasing rate in the magnitude of A' below 0.5 GPa is larger than that above 1 GPa. This fact suggests that the decrease in A' tends to saturate at high pressure. Roughly speaking, the decrease corresponds to a decrease of $D(\varepsilon_{\rm F})$ by applying pressure, since a change in $\Gamma/B_{\rm T}$ may be small at moderate pressure. In other words, the Kondo temperature $T_{\rm K}$ increases with increasing pressure because $D(\varepsilon_{\rm F})$ is proportional to $T_{\rm K}^{-1}$ (Kagayama and Oomi, 1996). The increase in $T_{\rm K}$ by applying pressure has been reported for many CK compounds (Kagayama and Oomi, 1996).

Electrical resistivity of CeNi at high pressure was reported by Oomi and Môri, 1994. The coefficients of T^2 term in the electrical resistivity have been found to decrease with increasing pressure. Considering that the coefficients are proportional to $D(\varepsilon_F)^2$ or T_K^{-2} , the DOSs at the Fermi level of CeNi decreases with increasing pressure. This result is the same as that mentioned above. Further, the above-mentioned result is supported by the results for the ternary alloy system (Ce_{1-x}La_x)Ni. The lattice constant of this alloy increases with *x*, which is considered as a negative pressure effect. It has been reported that the value of *A'* increases with *x* suggesting an increase in $D(\varepsilon_F)$: the value of *A'* of x = 0.5 is about twice that of CeNi (Uwatoko et al., 1993). Similar results have been also reported for CeBe₁₃ (Kagayama and Oomi, 1998).

3.5 MS under high pressure

Measurements of MS in metals and alloys give useful information not only about instabilities of magnetic moment but also about quadrupole interactions. There have been little data about MS of HF compounds. Zieglowski et al. (1986) reported that MS of HF compounds is large, which indicates instability of 4f electrons in magnetic field. The large MS is expected to be observed in magnetically or electronically unstable systems such as invar alloys, some actinide compounds (Honda et al., 2001; Oomi et al., 1993c), and other. As far as we know, there has been no systematic research on MS of HF compounds at high pressure. This is partly due to the technical difficulties in the measurement of MS at high pressure. Recently, we have measured MS of HF compounds at high pressure using strain gage method. Here, we show the results for two HF compounds, CeInCu₂ and CeAl₃ (Oomi and Kagayama, 1994).

Figure 72 shows an example of magnetostriction of CeInCu₂ at ambient pressure for the directions parallel λ_{\parallel} and perpendicular λ_{\perp} to the magnetic field *H*, where λ_i is defined as $\lambda_i = [l(H) - l(0)]/l(0)$, where l(H)and l(0) are the lengths of sample at *H* and H = 0, respectively. Both λ_{\parallel} and λ_{\perp} increase smoothly with increasing *H*. The volume MS is defined as $\lambda_V = \lambda_{\parallel} + 2\lambda_{\perp}$. The values of volume MS λ_V are shown in Figure 73 as a function of magnetic field at ambient pressure. The magnitude of λ_V is about 1×10^{-4} at 10 T, which is comparable with that of CeCu₆. The MS of CeInCu₂ under high pressure was measured only for the direction perpendicular to magnetic field.

 λ_{\perp} of CeInCu₂ at 4.2 K is shown in Figure 74 as a function of *H* at various pressures. Here, λ_{\perp} is defined as follows:

$$\lambda_{\perp}(P,H) = \frac{\Delta l}{l}(P,H) - \frac{\Delta l}{l}(P=2 \text{ GPa},H), \qquad (34)$$

where $\Delta l/l$ is the change in the length perpendicular to H. λ_{\perp} increases smoothly with increasing H up to 5 T similar to that at ambient pressure. The magnitude of $\lambda_{\perp}(P, H)$ decreases by applying pressure: the value of λ_{\perp}



FIGURE 72 Magnetostriction of CelnCu₂ parallel λ_{\parallel} and perpendicular λ_{\perp} to the direction of magnetic field at ambient pressure (Kagayama, 1995).



FIGURE 73 Volume magnetostriction of CelnCu₂ at 1.6 K and at ambient pressure (Kagayama, 1995).



FIGURE 74 λ_{\perp} of CelnCu₂ at various pressures (Oomi and Kagayama, 1994).

at 5 T are 180×10^{-6} and 50×10^{-6} at ambient pressure and at 1.2 GPa, respectively. The overall behavior of λ_{\perp} is similar to that of CeAl₃. The pressure coefficient of λ_{\perp} of CeInCu₂ is larger than that of CeAl₃. λ_{\perp} of CeInCu₂ and CeAl₃ at H = 1 T is several parts per million, which is about two orders of magnitude larger than that of IV compounds like CeBe₁₃ (Zieglowski et al., 1986). The large value of λ_{\perp} implies instability of magnetic state under external forces as is expected from thermodynamical equation, $\partial \lambda_{\perp} / \partial H \cong -\partial M / \partial P$, where *M* is the magnetization. This fact suggests that a pressure-induced electronic transition such as crossover, which we will point out in Section 4.1, may occur in these HF compounds. The large value of MS may be one of the characteristics of HF compounds.



FIGURE 75 Relative change of magnetostriction of CeAl₃ perpendicular to *H*, λ_{\perp} , as a function of *H* at 4.2 K under pressure (Oomi and Kagayama, 1994).

It is known that the λ_{\perp} may be written as $\lambda_{\perp} = aH^2$, and the value of *a* is proportional to $(T + T_K)^{-2}$ (Oomi et al., 1992; Zieglowski et al., 1986). Since T_K is enhanced largely by applying pressure, λ_{\perp} decreases with increasing pressure. The results in Figures 74 and 75 are consistent with this consideration. Thus the decrease in λ_{\perp} or *a* with increasing pressure is explained qualitatively by an increase of T_K at high pressure.

4. NEW ELECTRONIC PHASE TRANSITIONS UNDER HIGH PRESSURE

QPTs occur at 0 K in highly correlated electron systems due to variation of nonthermal control parameters which gives rise to a fundamental change in the ground state. The typical parameters to tune QPT are the chemical composition, pressure, or magnetic field. While phase transitions in classical models are driven only by thermal fluctuations and since classical systems usually freeze into a fluctuationless ground state at T = 0, quantum systems have fluctuations driven by the Heisenberg uncertainty principle even in the ground state. The T > 0 region in the vicinity of a QCP, however, offers a fascinating interplay of effects driven by quantum and thermal fluctuations. This means that working outward from QCP is a powerful way of understanding and describing the thermodynamic and dynamic properties of numerous systems in which QPT occurs. Indeed, unusual electronic and magnetic behaviors can arise near nonzero temperature (Löhneysen, 1999; Sachdev, 1999a,b). If the magnetic ordering temperature in a HF system is suppressed to absolute zero by tuning one or more of control parameters, magnetic fluctuations lead to strong enhancement of the quasiparticle scattering rate and potentially to a breakdown of the FL description. In this chapter, we show some examples of pressure-induced crossover and QPT in highly correlated materials mainly for HF systems and also pressure-induced new phenomena such as non-Fermi liquid (NFL) behavior and SC.

4.1 Pressure-induced crossover

In this section, as examples of pressure-induced crossover, we will show some data on electrical resistivity under pressure for three HF materials CeAl₃, CeAl₂, and CeInCu₂. Brief discussions about these novel electronic states induced by high pressure will be introduced.

4.1.1 CeAl₃

The temperature dependence of the electrical resistivity ρ of CeAl₃ at various pressures up to 8 GPa and ρ of LaAl₃ at ambient pressure are shown in Figure 76 (Kagayama and Oomi, 1996). The electrical resistivity of LaAl₃ is similar to the ordinary nonmagnetic metal; it varies linearly



FIGURE 76 The electrical resistivity, ρ , of CeAl₃ at high pressures as a function of temperature. ρ of LaAl₃ at ambient pressure is also shown for comparison (Kagayama and Oomi, 1996).

with temperature above 100 K without any anomalies. On the other hand, ρ of CeAl₃ at ambient pressure increases logarithmically with decreasing temperature until it reaches a maximum at 35 K and has a shoulder near 6 K. This behavior is due to the Kondo scattering on a thermally populated level split by CEF (Cornut and Coqblin, 1972). With increasing pressure, the peak and the shoulder merge into one peak, which is shifted toward higher temperatures. The ρ –T at 8 GPa becomes similar to that of LaAl₃. This result is interpreted as a pressure-induced crossover in the electronic state of CeAl₃ from a small- $T_{\rm K}$ HF state to a large- $T_{\rm K}$ IV state associated with an increase in the hybridization between the conduction band and 4f electrons.

In order to get the temperature-dependent 4f magnetic contribution ρ_{mag} , the ρ (LaAl₃) is assumed to be pressure-independent phonon part of CeAl₃ and subtracted from the ρ (CeAl₃) at various pressures, $\rho_{mag} = \rho$ (CeAl₃) – ρ (LaAl₃). Figure 77 illustrates the ρ_{mag} as a function of log *T*. The maximum temperature T_{max} in the ρ_{mag} increases with increasing pressure. Since T_{max} is roughly proportional to the T_{K} , the pressure



FIGURE 77 The magnetic part of the electrical resistivity, ρ_{mag} , of CeAl₃ as a function of log *T* at various pressures (Kagayama and Oomi, 1996).

dependence of $T_{\rm K}$ may be inferred. On the other hand, the logarithmic dependence of $\rho_{\rm mag}$ on temperature is observed in the wide range above $T_{\rm max}$. The negative slope becomes steeper at higher pressure reflecting the strong Kondo scattering with large enhancement of $T_{\rm K}$ at high pressure.

In order to examine the T^2 dependence in ρ_{mag} at low temperature, ρ_{mag} is plotted as a function of T^2 in Figure 78 up to 17 K for $P \le 1.5$ GPa and to 80 K for $P \ge 3$ GPa. Above 0.8 GPa, the T^2 dependence is clearly observed in these temperature ranges as shown by straight lines. As pressure increases, the slope decreases and the temperature range showing T^2 dependence becomes wider.

The coefficient *A* of the T^2 term is shown in Figure 79 as a function of pressure. The value of *A* is reduced by three orders of magnitude compared to that at ambient pressure, which was reported previously to be $35 \,\mu\Omega \,\mathrm{cm/K^2}$ (Andres et al., 1975). The rapid decrease in the magnitude of *A* is explained by the enhancement of $T_{\rm K}$ by applying pressure, which is



FIGURE 78 ρ_{mag} of CeAl₃ as a function of T^2 (Kagayama and Oomi, 1996).



FIGURE 79 The coefficient A of the T^2 term of CeAl₃ as a function of pressure (Kagayama and Oomi, 1996).

consistent with the increase in T_{max} because the coefficient *A* is inversely proportional to T_{K}^2 . These results are qualitatively consistent with the pressure dependence of specific heat coefficient γ as mentioned in Section 3.3.1. The value of γ decreases significantly with increasing pressure. Considering that γ is proportional to T_{K}^{-1} , the large decrease of γ corresponds to an enhancement of T_{K} by applying pressure.

4.1.2 CeAl₂

Figure 80A shows the temperature-dependent electrical resistivity ρ (CeAl₂) at various pressures and nonmagnetic LaAl₂, ρ (LaAl₂), at ambient pressure for comparison. At ambient pressure, $\rho(CeAl_2)$ decreases with decreasing temperature and shows a peak around 5 K and a shoulder around 60 K. The peak shifts to lower temperature and disappears above 2.5 GPa. On the other hand, the shoulder is enhanced at high pressure becoming a broad peak centered around 50 K at 3 GPa. The broad peak becomes less prominent by applying higher pressure. The magnetic part of the electrical resistivity ρ_{mag} was estimated by subtracting phonon contribution using the $\rho(\text{LaAl}_2)$, $\rho_{\text{mag}} = \rho(\text{CeAl}_2) - \rho(\text{LaAl}_2)$, where we assume that the phonon part of $\rho(\text{CeAl}_2)$ is approximated by ρ (LaAl₂). ρ _{mag} curves are shown in Figure 80B as a function of temperature in the logarithmic scale. ρ_{mag} at ambient pressure has two maxima due to combination of Kondo effect and CEF splitting, which were observed up to 2.4 GPa. These peaks become a single peak above 2.5 GPa through a shoulder in the ρ around 2.5 GPa. The temperatures of two maxima are defined as T_1 and T_2 . In Figure 80B, T_1 , T_2 , and the Nèel temperature T_N at ambient pressure are shown by arrows. ρ_{mag} at T_2 increases below 2.5 GPa with pressure, while it decreases above 2.5 GPa.



FIGURE 80 (A) Temperature dependence of the electrical resistivity of CeAl₂ under high pressure. (B) The temperature dependence of ρ_{mag} . T_1 , T_2 , and T_N at ambient pressure were shown by arrows (Miyagawa et al., 2008).

Figure 81 shows the pressure dependence of T_1 , T_2 , and T_N . T_N decreases with increasing pressure. Extrapolation of the data results in a critical pressure at around 3 GPa for a disappearance of the magnetism.



FIGURE 81 T_1 , T_2 , and T_N of CeAl₂ as a function of pressure. The closed circles show the pressure dependence of T_1 and T_2 . The open squares show T_N as a function of pressure. The dashed line is guide to the eye (Miyagawa et al., 2008).



FIGURE 82 $\rho(T)$ of CeAl₂ under high pressure down to 50 mK (Miyagawa et al., 2008).

 T_1 decreases with pressure and has a minimum value at 2.1 GPa. At higher pressures, T_1 begins to increase strongly indicating that T_1 merges to T_2 . It is interesting to note that T_2 decreases with pressure below 3 GPa but begins to increase above 3 GPa. Similar behavior for T_1 and T_2 has been reported in other Ce compounds such as CeCu₂Si₂ (Holmes et al., 2004) and CeCu₂Ge₂ (Jaccard and Holmes, 2005).

Figure 82 shows the detailed behavior of ρ below 15 K. Electrical resistivity changes significantly as pressure increases: ρ at 2.1 GPa has a

broad peak around 4 K followed by a rapid decrease below that due to magnetic ordering, but as pressure increases, the peak disappears, and then ρ above 2.6 GPa shows a smooth increase with temperature. The electronic state near QCP is different from the normal FL behavior showing T^2 dependence in the electrical resistivity. Here, it was attempted to fit the temperature dependence of the electrical resistivity to the following equation:

$$\rho_{\rm mag} = \rho_0 + A_n T^n, \tag{35}$$

where ρ_0 , A_n , and n are the residual resistivity, the coefficient, and exponent related to electronic state, respectively.

 $\rho_{\rm mag}$ below 2 K is shown in Figure 83. Fitting was carried out in the temperature range 50 mK < *T* < 2 K. Solid curves in Figure 83 show the result of fitting, in which these curves reproduce well the experimental data.

Figure 84 shows the pressure dependence of ρ_0 and n. ρ_0 has a peak around 2.7 GPa. n is 2 below 2 GPa but around 2.7 GPa, it is 1.3–1.4, which significantly deviates from the normal FL behavior (n = 2). Judging from these facts, it is concluded that CeAl₂ shows the QPT around 2.7 GPa. This indicates that the electronic state around 2.7 GPa is the so-called NFL state. Further, n becomes 2 above 3 GPa (Miyagawa et al., 2008), indicating that the FL behavior is recovered.

Figure 85 shows the pressure dependence of the electrical resistivity at several temperatures in the range 2.6 < T < 300 K, which was obtained from the results shown in Figure 80A. For all the isothermal ρ -P curves,



FIGURE 83 Temperature dependence of ρ_{mag} of CeAl₂ below 2 K at high pressure. Solid curves show the results of fitting (Miyagawa et al., 2008).



FIGURE 84 ρ_0 and *n* of CeAl₂ as a function of pressure. The solid curves are drawn as guide to the eye (Miyagawa et al., 2008).

ρ increases with pressure followed by a maximum, $ρ_{max}$, at $P = P_{max}$ and P_{max} increases with temperature. We also observed similar behavior for CeAl₃ as shown in Figure 11 in Section 2.1.3.1. $ρ_{max}$ is clear at low temperature (T < 35 K) but the maximum become broad at high temperature (T > 85 K). It has been reported that there is a crossover induced by pressure from weak Kondo (small $T_{\rm K}$) to strong Kondo (large $T_{\rm K}$) regime, which is largely different from the first-order γ-α phase transition in Ce metal (Barbara et al., 1986). In such a sense, the peaks observed in Figure 85 may correspond to the crossover in the electronic state of CeAl₂. $P_{max}-T$ curve indicates that the Kondo temperature $T_{\rm K}$ increases with increasing pressure. P_{max} is plotted in Figure 86. P_{max} increases gradually up to 2.6 GPa, and then rapidly above the pressure where T_2 also shows a similar change and then crosses room temperature at 5.5 GPa.

In summary, $T_{\rm K}$ increases with pressure while $T_{\rm N}$ is decreased by applying pressure and expected to disappear around 2.7 GPa. Since the coefficient of the T^2 term diverges around 2.7 GPa, the magnetic phase



FIGURE 85 Pressure dependence of the electrical resistivity of $CeAl_2$ at several temperatures. The filled circles are obtained by isobaric temperature-dependent data at several pressures. The thick line shows isothermal pressure dependence of the electrical resistivity at 290 K (Miyagawa et al., 2008).



FIGURE 86 T-P phase diagram of CeAl₂ obtained from data discussed in Section 4.1.2 (Miyagawa et al., 2008). The filled circles show the pressure P_{max} showing the maximum of $\rho-P$ curves as shown in Figure 85. The open circles show the pressure dependence of T_1 and T_2 for comparison with P_{max} .

boundary exists at 2.7 GPa where NFL behavior is observed in $\rho(T)$. Above 3 GPa, the pressure effect on T_2 changes and FL behavior is recovered.

4.1.3 CelnCu₂

The temperature dependence of electrical resistivity ρ of CeInCu₂ at various pressures up to 8 GPa is shown in Figure 87. At ambient pressure, ρ increases gradually with decreasing temperature, reaches a maximum around 27 K, and then decreases rapidly on further cooling. This behavior is similar to those of typical HF compounds (Brandt and Moshchalkov, 1984). The residual resistivity ρ_0 decreases rapidly with increasing pressure, which is different from the pressure dependence of ρ_0 for CeCu₆ (Kagayama et al., 1991a). The temperature T_{max} of the resistivity maximum increases with increasing pressure and then the maximum in the ρ -*T* curve, which is a characteristic of CK system (CKS), is not observed above 4.5 GPa in the temperature range of Figure 87. Since a large increase in T_{max} corresponds to an increase in T_{Kr} as will be mentioned in the following section, the change in the overall behavior in the ρ -*T* curve in Figure 87 implies a crossover from an HF at low pressures to an IV state at high pressures (Lavagna et al., 1983). Such crossover has also been observed in some cerium and uranium compounds (Aronson et al., 1989; Bellarbi et al., 1984; McElfresh et al., 1990; Ponchet et al., 1986; Yomo et al., 1988).



FIGURE 87 Electrical resistivity ρ of CelnCu₂ at high pressures as a function of temperature (Kagayama et al., 1992a).

In order to examine the T^2 dependence in the ρ , which is characteristic of a FL, $\rho - \rho_0$ is plotted as a function of T^2 as shown in Figure 88. $\rho - \rho_0$ has a T^2 dependence at low temperatures. As the pressure increases, the temperature range in which ρ shows the T^2 dependence becomes wider. The values of A and T_{max} are shown in Figure 89 as functions of pressure. It is seen that A decreases rapidly with increasing pressure below about 3 GPa, and the rate of decrease becomes small at high pressures. On the contrary, T_{max} increases rapidly with increasing pressure; T_{max} is 27 K at ambient pressure, but it increases to 300 K around 3.8 GPa.

It is well known that T_{max} is roughly proportional to T_{K} and that the value of A depends on T_{K} as $A \propto T_{\text{K}}^{-2}$ (Ponchet et al., 1986; Wire et al., 1984; Yoshimori and Kasai, 1983). Thus T_{max} is inversely proportional to \sqrt{A} . To examine this relation, the value of $1/\sqrt{A}$ is plotted as a function of T_{max} in Figure 90. The value of $1/\sqrt{A}$ shows a linear dependence on T_{max} . The rapid decrease in A observed in Figure 89 arises from the large increase in T_{max} or T_{K} at high pressures, which is induced by the increase in the hybridization between 4f electrons and the conduction band. This indicates that A and T_{max} are dominated by a single energy scale T_{K} .



FIGURE 88 $\rho - \rho_0$ versus T^2 of CeInCu₂ (A) below 2 GPa and 7 K and (B) above 1.5 GPa and below 40 K: the solid lines show the T^2 dependence (Kagayama et al., 1992a).



FIGURE 89 (A) The resistivity-maximum temperature T_{max} of CelnCu₂, (B) the coefficient A of the T^2 term as a function of pressure (Kagayama and Oomi, 1996).



FIGURE 90 $1/\sqrt{A}$ plotted against T_{max} for CeInCu₂ and CeCu₆ (Kagayama and Oomi, 1993b).

Next, Grüneisen parameter Γ for T_{max} is discussed. Extremely large values of Γ , as high as 50, have been reported for HF compounds (Visser et al., 1990), while it is of the order of 1 for normal metals. The Γ for T_{max} , $\Gamma(T_{\text{max}})$ is defined as:

$$\ln\left[\frac{T_{\max}}{T_{\max}(0)}\right] = -\Gamma \ln\left(\frac{V}{V_0}\right). \tag{36}$$



FIGURE 91 $\ln[T_{max}(P)/T_{max}(0)]$ of CelnCu₂ as a function of volume (Kagayama et al., 1994c).

Since $T_{\text{max}} \sim T_{\text{K}}$, this equation is the same as Eq. (3) in Section 2. Figure 91 shows a plot of $\ln[T_{\text{max}}(P)/T_{\text{max}}(0)]$ as a function of volume. The pressure coefficient of relative change of T_{max} , $\partial(\ln T_{\text{max}})/\partial P$ is about 0.69 GPa⁻¹. Γ is determined to be 62.5 by substituting the observed value of κ , 11×10^{-3} GPa⁻¹ (Kagayama et al., 1990). In Table 1, we summarize the values of $\partial(\ln T_{\text{max}})/\partial P$, κ , and Γ , for CeInCu₂, CeCu₆, CeA1₃, and CePd₃. The Γ values of three HF compounds are larger than those of IVS compounds such as CePd₃, $\Gamma = 9$ (Oomi et al., 1990a). Large values of Γ have been observed for other HF compounds including uranium compounds (Visser et al., 1990). Taking into account these results, the large Γ value seems to be one of the characteristics of HF compounds.

Figure 92 illustrates the relative change of the $T_{\rm K}$ or the coefficient $A \propto T_{\rm max}^{-2}$ of CeInCu₂, CeAl₃, and URu₂Si₂ (Kagayama and Oomi, 1995, 1996; Kagayama et al., 1994b) as functions of volume. The origin of this plot is adjusted appropriately using the Γ value at ambient pressure, and the rectangle shows the range of the measurements of $T_{\rm K}$ and V, that is, 0 < P < 8 GPa. The range of the horizontal axis of each rectangle depends on the magnitude of bulk modulus B_0 ; it becomes wider with smaller value of B_0 . The slope of this curve is the Grüneisen parameter at nonambient pressure. It is seen that the magnitude of the slope becomes smaller as pressure increases. In other words, the volume-dependent Grüneisen parameter decreases with increasing pressure, which corresponds to a crossover induced by pressure. The magnitudes of $\Gamma(T_{max})$ at ambient pressure are summarized in Table 4. All observed points for the three HF materials fall on a "universal" curve, which is depicted using a solid curve in Figure 92. This fact suggests that the present treatment is a useful tool to analyze quantitatively the pressure dependent ρ curve.



FIGURE 92 Relative change of the $T_{\rm K}$ versus volume in logarithmic scale for three HF compounds. The observed points of three HF compounds fall on a "universal curve" that is shown using the solid line (Kagayama, 1995).

TABLE 4 T_{max} , γ , and Γ (T_{max}) for CelnCu₂ (Kagayama and Oomi, 1993b; Kagayama et al., 1990, 1992b), CeCu₆ (Kagayama and Oomi, 1993c; Kagayama et al., 1991a; Oomi et al., 1988a,b), CeAl₃ (Kagayama and Oomi, 1996; Oomi and Kagayama, 1996; Percheron et al., 1973; Takke et al., 1980) and CePd₃ (Oomi et al., 1990b)

	T _{max} (K)	γ (mJ∕mol K²)	Г (T _{max})
CelnCu ₂	27	1200	59
CeCu ₆	15	1500	65
CeA1 ₃	35	1500	97
CePd ₃	100	39	8.6

Further, the applicability of this treatment should be examined for other HF and IV compounds.

4.2 Pressure-induced SC

In this section, as example of pressure-induced SC, we will show some electrical, magnetic, and thermal properties of CeRh₂Si₂, CePtSi₂, and UGe₂ under pressure. Similarity and difference in the pressure-induced new electronic phase in three materials will be pointed out. The conditions for the occurrence of pressure-induced SC are explored.

4.2.1 CeRh₂Si₂

As mentioned in Sections 2.1.3.2 and 3.4.2.1, CeRh₂Si₂ is a typical Kondo compound. The temperature dependence of magnetic susceptibilities for H = 1 T along the *a*-axis, χ_a , and *c*-axis, χ_c , at ambient pressures is shown in



FIGURE 93 Temperature dependence of the anisotropic magnetic susceptibility of CeRh₂Si₂ at ambient pressure (Mori et al., 1999).

Figure 93 (Mori et al., 1999). The magnetic susceptibilities χ_a and χ_c exhibit two anomalies at T_{N1} and T_{N2} . At low temperatures, the susceptibility increases slightly with decreasing temperature for both directions. This increase in susceptibility at low temperature may be due to a small amount of impurity.

Figure 94A and B shows the temperature dependence of the magnetic susceptibilities χ_a and χ_c at various pressures. For all pressures, χ_c exhibits a sharp drop at the antiferromagnetic transition, which occurs just below the maximum in the susceptibility. The size of the anomaly due to the magnetic transition at T_{N1} decreases with increasing pressure. On the other hand, T_{N2} decreases linearly with increasing pressure and is no longer seen at high pressure in χ_a . The maximum of χ_c that indicates the Kondo temperature (Smith and Chu, 1967) increases with increasing pressure at a rate of $dT_{max}/dP = dT_K/dP = 0.046$ K GPa⁻¹. The value of χ_c is about 4.5 times larger than χ_a at $T_{N1} = 36$ K under ambient pressure. This anisotropy decreases by a factor of 2 at 1 GPa, suggesting that the magnetic anisotropy may decrease with increasing pressure.

Figure 95 shows the electrical resistivity $\rho(T)$ for *a*- and *c*-axes as a function of temperature below 40 K under high pressures. At ambient pressure, the resistivity shows a sudden decrease near 35 K (= $T_{\rm N1}$). Moreover, the resistivity shows a small anomaly at 24 K (= $T_{\rm N2}$). The anomalies at $T_{\rm N1}$ and $T_{\rm N2}$ correspond to the magnetic phase transitions which were mentioned before. The anomaly near $T_{\rm N1}$ becomes less prominent with increasing pressure, corresponding to the pressure-induced decrease of the sublattice magnetization (Kawarazaki et al., 2000). $T_{\rm N1}$ decreases with increasing pressure and disappears above 1.0 GPa (~ $P_{\rm c1}$).

 $T_{\rm N2}$ also decreases with increasing pressure and disappears above 0.58 GPa (~ $P_{\rm c2}$). At 0.4 GPa, on the other hand, $\rho(T)$ shows a minimum



FIGURE 94 Temperature dependence of the anisotropic magnetic susceptibility in CeRh₂Si₂ at various pressures along (A) *c*- and (B) *a*-axes (Mori et al., 1999).

at $T_{N2} \sim 14.5$ K along the *a*- and *c*-axes. Further, as seen in Figure 96, the hysteresis is observed near T_{N2} along the *a*-axis, indicating that this transition is first order. Although no hysteresis is observed at ambient pressure, the results of quasielastic neutron scattering indicate that this transition is first order at ambient pressure (Graf et al., 1998; Severing et al., 1989).

The magnetic phase transition temperatures, T_{N1} and T_{N2} , were determined by calculating the temperature derivatives of $\rho(T)$, $d\rho/dT$. The pressure dependence of T_{N1} and T_{N2} , plotted in Figure 97, is in good agreement with that determined by the measurements of thermal expansion (Figure 57; Honda et al., 1999). T_{N1} decreases gradually at low pressure and then abruptly near 1 GPa, which is the critical pressure P_{c1} where the transition disappears. Qualitatively, the phase boundary of T_{N1} is interpreted on the basis of Doniach's model for competing Kondo and RKKY interactions (Doniach, 1977). From the dHvA experiment under high pressure, the topology of the Fermi surface changes abruptly above 1.1 GPa (Araki et al., 2001). Since a new Fermi surface under high pressure



FIGURE 95 Temperature dependence of the electrical resistivity of $CeRh_2Si_2$ along the a- and c-axes (Ohashi et al., 2003a).



FIGURE 96 The electrical resistivity of CeRh₂Si₂ below 20 K at 0.4 GPa (Ohashi et al., 2003a).



FIGURE 97 Pressure dependence of the critical temperatures T_{N1} and T_{N2} of CeRh₂Si₂. Broken lines are guide to the eye (Ohashi et al., 2003a).

is explained by the 4f-itinerant-band model, it is concluded that a change in the 4f electronic state from a 4f-localized Fermi surface to a 4f-itinerant Fermi surface occurs.

SC in CeRh₂Si₂ was first discovered by Movshovich et al. (1996) for a polycrystalline sample in the pressure range above P_{c2} from 0.6 to 1.6 GPa. The low-temperature resistivity for a high-quality single-crystal sample is shown in Figure 98 (Settai et al., 2007). An indication of SC appears in the pressure region from 0.97 to 1.20 GPa; the zero resistivity is observed only at P = 1.05 and 1.06 GPa at 0.42 K. This implies that homogeneous bulk SC is realized in an extremely narrow pressure region around P_{c1} .

The resistivity ρ follows the FL form $\rho(T) = \rho_0 + AT^2$ at low temperature in a wide pressure range, where ρ_0 is the temperature-independent residual resistivity and *A* is the constant. Figure 99 shows the T^2 dependence of ρ - ρ_0 below 2.3 GPa along *a*- and *c*-axes. The T^2 dependence is observed even around P_{c1} and P_{c2} . This is a characteristic feature of CeRh₂Si₂.

The values of *A* for *a*- and *c*-axes are shown in Figure 100 as a function of pressure. It is found that *A* shows a maximum near 1.0 GPa for the current along the *a*-axis and near 0.86 GPa along the *c*-axis. This indicates that the value *A* exhibits a peak at the critical pressure P_{c1} between 0.86 and 1.0 GPa, pointing to strong spin fluctuations which corresponds to the pressure-induced QPT. It is noted that anisotropy for the value of *A* changes drastically at P_{c1} . The inset in Figure 100 shows the pressure dependence of the ratio A_a/A_c . A discontinuity is observed at the critical pressure P_{c1} , indicating that this transition changes the topology of the Fermi surface. On the other hand, no anomaly is observed near P_{c2} . Since this transition is first order, no fluctuations may exist and then the coefficient *A* is not affected.

1.0

0.5 (μΩ cm)

1.01

0

0



0.4 Temperature (K) 1.06 1.05

0.6

FIGURE 98 Low-temperature resistivity under pressure near P_{c1} of CeRh₂Si₂ (Araki et al., 2003; Settai et al., 2007).

0.2

Qualitatively, the pressure dependence of *A* is consistent with that of Sommerfeld coefficient γ of specific heat. As shown in Figures 101 and 102, γ increases from 20 mJ/mol K² at ambient pressure and passes through a broad maximum of 80 mJ/mol K² near 1.0 GPa. In the general case, the coefficient *A* of *T*² term in the resistivity and the linear specific heat coefficient γ appear to have the relation $A \propto \gamma^2$ (Kadowaki and Woods, 1986; Miyake et al., 1989). For HF compounds, the value of $A/\gamma^2 = 1.0 \times 10^{-5} \,\mu\Omega \,\text{cm/(mJ/mol K)}^2$ supports the viewpoint that the heavy mass is essentially due to the many-body dynamical effect between the lattice of local moments and the light conduction electrons. On the other hand, a small value $A/\gamma^2 \sim 0.4 \times 10^{-6} \,\mu\Omega \,\text{cm/(mJ/mol K)}^2$ is observed in ordinary transition metals, which is due to a peculiar property of a single band.

Figure 103 shows the value of A/γ^2 as a function of pressure. The value of γ is taken from the result of specific heat under pressure (Graf et al., 1997). The ratio A/γ^2 is found to depend on pressure since the behavior of A is different quantitatively from that of γ . The dashed line indicates the universal value $A/\gamma^2 \sim 0.4 \times 10^{-6} \,\mu\Omega \,\mathrm{cm/(mJ/mol K)^2}$ typical for ordinary transition metals (Miyake et al., 1989). At ambient pressure, we find



FIGURE 99 T^2 dependence of $\Delta \rho = \rho - \rho_0$ of CeRh₂Si₂ along the *a*- and *c*-axes (Ohashi et al., 2003a).



FIGURE 100 Pressure dependence of the coefficient of T^2 of CeRh₂Si₂ along the *a*- and *c*-axes. Solid lines are guide to the eye. The inset shows the ratio A_{α}/A_c as a function of pressure (Ohashi et al., 2003a).



FIGURE 101 Magnetic specific heat $C_m \operatorname{CeRh}_2\operatorname{Si}_2$ divided by temperature as a function of temperature represented on a logarithmic scale at various pressures (Graf et al., 1997). The lattice specific heat of $\operatorname{CeRh}_2\operatorname{Si}_2$ was approximated by that of $\operatorname{LaRhRuSi}_2$ (Calemczlk, 1990) and subtracted from the total specific heat to obtain C_m . The inset is a plot of C_m/T versus T for $\operatorname{CeRh}_2\operatorname{Si}_2$ at ambient pressure (open circles). The solid curve in the inset is the magnetic entropy S_m , calculated as the integral of C_m/T , and the dotted horizontal line corresponds to $R \ln 2$.



FIGURE 102 Electronic specific heat coefficient γ of CeRh₂Si₂ as a function of pressure. The inset is a plot of $T_N(P)$ normalized to its P = 0 value for two different samples. In both cases, the dotted lines are guides to the eye (Graf et al., 1997).



FIGURE 103 Pressure dependence of the ratio of A/γ^2 of CeRh₂Si₂ along the *a*- and *c*-axes. Broken lines are guide to the eye (Ohashi et al., 2003a).

 $A/\gamma^2 \sim 3.5 \times 10^{-6}$ along the *a*-axis and 2.1×10^{-6} along the *c*-axis; these values are larger than that of transition metals by one order of magnitude. This indicates that effect of magnetic scattering merges into the *A* and γ value. At low pressures below 0.4 GPa, A/γ^2 decreases rapidly with increasing pressure, which comes from the vanishing of magnetic order. Above 0.6 GPa, however, A/γ^2 increases strongly with pressure below 0.9 GPa having a peak around 1 GPa. Moreover, it decreases again with pressure up to 1.7 GPa, at which point A/γ^2 because $\sim 1.0 \times 10^{-6}$ along the *a*-axis and 0.5×10^{-6} along the *c*-axis, which are almost the same as that of transition metals. These data indicate that nonmagnetic scattering exists at the critical pressure *P*_{c1}, and that a crossover from a HF state to an IV state occurs at high pressure.

Such behavior has been observed in the ferromagnetic U-compound UGe₂ (Oomi et al., 1998, 2000; Tateiwa et al., 2001). It shows a ferromagnetic ordering at $T_{\rm C} = 52$ K at ambient pressure. Both $T_{\rm C}$ and $T_{\rm x}$, the latter is a characteristic transition temperature observed below $T_{\rm C}$, decrease with increasing pressure and become zero around 1.9 and 1.2 GPa, respectively. At low pressures below 1 GPa, the value of $A/\gamma^2 \sim 1.0 \times 10^{-5}$ is near the empirical universal value for HF systems. Up to 1.1 GPa, A/γ^2 decreases to 1.0×10^{-6} , where the transition characterized by $T_{\rm x}$ disappears. Moreover, A/γ^2 increases strongly again to 9×10^{-6} up to 1.3 GPa, where the value of A shows a peak. These anomalies are related closely with the occurrence of SC. In other words, these anomalies are regarded as a precursor for the pressure-induced SC.

Next, the values of the residual resistivity ρ_0 for *a*- and *c*-axes are shown in Figure 104 as a function of pressure. For both the *a*- and *c*-axes, ρ_0 increases slightly as pressure increases and then decreases



FIGURE 104 Pressure dependence of the residual resistivity of ρ_0 of CeRh₂Si₂ along the *a*- and *c*-axes. Solid lines are guide to the eye (Ohashi et al., 2003a).

exhibiting a minimum near 0.6 GPa ~ P_{c2} , where the magnetic phase transition disappears. The result indicates that the critical point near P_{c2} affects the magnitude of ρ_0 . On the other hand, it is difficult to show whether an anomaly on ρ_0 exists near P_{c1} . In the case of ferromagnetic QCP, the anomaly of ρ_0 is expected to be observed at the critical point, while the less pronounced anomalies expected in the case of AF-QCP (Miyake and Narikiyo, 2002).

Figure 105 shows the temperature dependence of the electrical resistivity over a wide temperature range at high pressures up to 8 GPa. No anomaly was detected in the ρ -T above 1.5 GPa, since magnetic ordering was suppressed completely. Instead, an inflection point at $T_{\rm m}$ is observed in the ρ curve above 1.5 GPa. $T_{\rm m}$ shifts rapidly from 44 K at 1.5 GPa to higher temperature with increasing pressure.

 T^2 dependence was observed at low temperature below T_m . The coefficient A_a decreases significantly with increasing pressure: the value of A_a at 8 GPa is smaller than the same at 1.5 GPa by two orders of magnitude. Figure 106 shows the pressure dependence of the value of A_a and $1/T_m^2$ up to 8 GPa. It is found that the pressure versus A curve is proportional to that for $1/T_m^2$, that is, A is approximately proportional to $1/T_m^2$ above P_{c1} . According to the theory of Yoshimori and Kasai (1983), the value of $A \propto 1/T_m^2$ is valid in the HF materials (Kagayama et al., 1991a). These facts indicate that T_m is proportional to T_K , $T_m \propto T_K$ (Yoshimori and Kasai, 1983).

 $T_{\rm K}$ is also estimated from the the temperature where magnetic susceptibility shows a peak. At ambient pressure, $T_{\rm K}$ is approximately 35 K, and it increases with pressure (Mori et al., 1999). The slope of $dT_{\rm K}/dP$ is calculated to be 0.046 K GPa⁻¹ from the result up to 1 GPa, while the large value is obtained, $dT_{\rm m}/dP > 15$ K above 1.5 GPa in the present work. It is



FIGURE 105 Temperature dependence of the electrical resistivity of $CeRh_2Si_2$ along the *a*-axis up to 8 GPa (Ohashi et al., 2003a).



FIGURE 106 A_a and $1/T_m^2$ of CeRh₂Si₂ as a function of pressure. Solid lines are guide to the eye to show that the curve of A versus P is nearly parallel to $1/T_m^2$ versus P curve (Ohashi et al., 2003a).

considered that below P_{c1} , two kinds of interactions, RKKY interactions and the Kondo effect, are competing with each other, and T_K is related not only to the Kondo effect but also to the RKKY interactions. Above P_{c1} , where the antiferromagnetic interactions disappear, T_K is expected to become pressure sensitive as in a typical nonmagnetic HF compound.

4.2.2 CePtSi₂

In Ce-based heavy compounds, various interesting phenomena such as non-BCS SC and (NFL) behavior occur due to competition between the RKKY interactions and the Kondo effect. CePtSi₂ has the CeNiGe₂-type orthorhombic layered structure (space group *Cmcm*), where the Ce and Pt–Si layers are stacked alternatively along the *b*-axis, with lattice constants a = 4.288, b = 16.718, and c = 4.238 Å (Geibel et al., 1992). The compound has the electronic specific heat coefficient γ in the paramagnetic state of 600 mJ/mol K² (Geibel et al., 1990; Lee et al., 1990), and the characteristic Kondo temperature $T_{\rm K}$ of 3 K, indicating that CePtSi₂ is a typical HF compound. Below $T_{\rm N} = 2$ K, an AF transition occurs, as indicated by a downward slope in the electrical resistivity and a jump in the specific heat (Geibel et al., 1990, 1992; Lee et al., 1990; Nakano et al., 2009a; Oomi et al., 1999). The $T_{\rm K}$ and $T_{\rm N}$ values indicate that the Kondo effect and RKKY interactions compete with each other in this compound.

From the high-pressure X-ray diffraction, the CeNiGe₂-type structure is confirmed to be stable at least up to 6 GPa at room temperature. The lattice constants decrease continuously with increasing pressure. The pressure dependence of relative volume V/V_0 is displayed in Figure 107. The solid line is the result of least-squares fit to the Murnaghan's equation (see Eq. (1)). B_0 and B_0' are evaluated to be 119 GPa and 3.0. These are in agreement with typical CK or HF compound such as CelnCu₂ ($B_0 = 90$ GPa, and $B_0' = 3.9$). Absence of a significant anomaly in V/V_0-P curve indicates that the crossover from the CK state or HF state (small T_K) to the IV state (large T_K) occurs gradually in CePtSi₂.

Figure 108 displays the temperature dependence of thermal expansion coefficient α at ambient pressure. α of CePtSi₂ is found to be the same as



FIGURE 107 The pressure dependence of volume of CePtSi₂ at room temperature. The solid line is least-squares fit to the first-order Murnaghan's equation (Eq. (1)) (Oomi et al., 1994a).



FIGURE 108 Thermal expansion coefficient α of CePtSi₂ and LaPtSi₂, as a function of temperature at ambient pressure (Oomi et al., 1993d).



FIGURE 109 α/T versus T^2 plot for CePtSi₂ and LaPtSi₂ (Oomi et al., 1993d).

that of LaPtSi₂ above 60 K but shows a minimum around 22 K. The increase in α/T at low temperature is well known as one of the characteristic behaviors of CK or HF compounds (Oomi et al., 1990a,c). α is generally described at low temperature as described in Eq. (25). The α/T versus T^2 plot is shown in Figure 109. A large enhancement in α/T is seen below 20 K. The value of α/T at 10 K is about 2.1×10^{-7} K⁻², which is much larger than that of LaPtSi₂, ~0.05 × 10⁻⁷ K², but is smaller than those of other HF materials such as CeAl₃, 6×10^{-7} K⁻² (Kagayama and Oomi, 1993a). This indicates a large effective-mass (m^*) enhancement or a high DOSs at the Fermi level $D(\varepsilon_F)$ due to the existence of 4f electrons; moreover, m^* of CePtSi₂ may be smaller than that of CeA1₃. This result agrees with the γ value of 600 mJ/mol K², which is smaller than that of CeAl₃, $\gamma = 1620$ mJ/mol K² (Andres and Graebner, 1975).

Figure 110A shows the Δ*l*/*l* of CePtSi₂ below 10 K measured by a capacitance method (Nakano et al., 2009b). Δ*l*/*l* decreases monotonously with decreasing temperature down to 2.5 K. It increases rapidly below 2 K, due to antiferromagnetic ordering. The α in low-temperature region is shown in Figure 110B. α of 2×10^{-6} (K⁻¹) at 10 K is consistent with that measured by a strain gage method in Figure 108 and is almost independent of the temperature down to 4 K. α decreases rapidly below 4 K and becomes negative below 2.4 K. α below 1.2 K becomes -6.5×10^{-6} (K⁻¹).



FIGURE 110 (A) Temperature dependence of the thermal expansion and (B) thermal expansion coefficient α of a polycrystalline sample of CePtSi₂. Inset: α/T as a function of *T* (Nakano et al., 2009b).

Similar behaviors have been observed in other antiferromagnetic Ce-based HF compounds, such as $CePd_2Si_2$ (Dijk van et al., 2000), $CeCu_6$ (Tsujii et al., 2000), and Ce_2RhIn_8 (Malinowski et al., 2003).

 α/T of CePtSi₂ at low temperatures is shown in the inset of Figure 110B. Below 10 K, α/T increases and shows a maximum at $T_{max} = 3.6$ K, which is almost consistent with $T_{\rm K}$ rather than with $T_{\rm N}$. Thus, this maximum would appear to be due to the Kondo effect, indicating development of hybridization between the conduction band and the 4f orbital. Below 2.1 K, α/T rapidly decreases due to the antiferromagnetic ordering.

 ρ of CePtSi₂ polycrystalline sample under pressure up to 8 GPa is shown in Figure 111. At ambient pressure, ρ increases with decreasing temperature and shows maxima around $T_1 = 5.4$ and $T_2 = 28.5$ K. Above 2 GPa, these maxima merge into a single one which shifts to higher pressure with increasing pressure, indicating increase of $T_{\rm K}$.

These two maxima are well known as characteristic features of Ce-based Kondo compounds, typical of interplay between the Kondo effect and CEF. At 8 GPa, FL like T^2 dependence appears up to 50 K. Similar behavior in the ρ –T curve at high pressure has been observed in other Ce compounds, which is interpreted as a pressure-induced crossover from the CK state or HF state (small $T_{\rm K}$) to the IV state (large $T_{\rm K}$).

In the temperature range 2 < T < 10 K, ρ_{mag} shows log T dependence as shown Figure 112 (Oomi et al., 1998). The log T dependence seems to



FIGURE 111 ρ -*T* curves of CePtSi₂ at various pressures up to 8 GPa. ρ -*T* curve of LaPtSi₂ is also shown for comparison (Oomi et al., 1994a).



FIGURE 112 The ρ_{mag} as a function of temperature on the logarithmic scale. The solid lines indicate log *T* dependence (Oomi et al., 1999).

become wider and steeper as pressure increases up to 3 GPa. This is different from the normal FL behavior, suggesting that $CePtSi_2$ is in NFL state between 1.5 and 4 GPa.

Figure 113 shows *C*/*T* under pressure up to 0.57 GPa. It shows a maximum around $T_{\rm N} = 1.8$ K due to the AFM order (Oomi et al., 1999). This maximum shifts to lower temperature with a rate of $dT_{\rm N}/dP = 1.5$ K GPa⁻¹; thus, the AFM order is expected to disappear and QCP should occur around 1 GPa.

The details of ρ have been measured down to 50 mK under pressure by Nakano et al. (2009a), and these are displayed in Figure 114A. At ambient pressure, ρ increases with decreasing temperature from 300 K and shows two maxima at 23 K (= T_2) and 7 K (= T_1). This is almost consistent with that shown in Figure 111. ρ shows a sharp decrease at $T_N = 1.8$ K due to the AF transition followed by FL like T^2 dependence below 1 K.

The pressure clearly changes the overall features in ρ . $T_{\rm N}$ decreases with increasing pressure up to 0.79 GPa, as shown in the inset of


FIGURE 113 Specific heat of CePtSi₂ at high pressure. T_{NS} are shown by arrows (Oomi et al., 1999).

Figure 114B. The pressure dependence of $T_{\rm N}$, $dT_{\rm N}/dP$, is found to be -0.9 K GPa⁻¹. The AF anomaly disappears above 0.9 GPa, displaying a deviation from the linear pressure dependence of T_N as shown in Figure 115A. Instead of the AFM anomaly, another abrupt resistivity drop due to the superconducting transition appears around 0.15 K above $P_{c1} = 1.4$ GPa. This resistivity drop develops with increasing pressure up to 1.7 GPa and is observed up to $P_{c2} = 2.1$ GPa. ρ with a low electric current of 10 µA at 1.7 GPa is shown in the inset of Figure 114A. It drops more sharply than that with 100 μ A and is expected to be close to zero below 50 mK. Figure 116 shows the low-temperature resistivity at 1.7 GPa with magnetic fields up to 0.7 T, parallel to the excitation current direction. The resistivity drop is suppressed by magnetic field and disappears above 0.7 T. This is a further direct evidence of the superconducting transition in CePtSi₂. Field dependence of T_c is displayed in the inset (A) of Figure 116. The upper critical field H_{c2} is found to be 0.7 T at 1.7 GPa. H_{c2}/T_c is evaluated to be 5 T/K, which is clearly larger than the Pauli limit of 1.86 T/K predicted by the BCS theory.

The ac susceptibility χ_{ac} for the same sample at 1.8 GPa is shown in the inset (B) of Figure 116: χ_{ac} drops below $T_c \sim 0.12$ K, which is consistent with that evaluated from the resistivity measurements. This is also a clear evidence of superconducting ordering. These drop and T_c are suppressed by the application of magnetic field and disappear above 0.3 T as shown



FIGURE 114 (A) Temperature dependence of the resistivity of CePtSi₂ under hydrostatic pressure. Inset: Details of resistivity around T_c at 1.7 GPa measured with a low excitation current. (B) Resistivity of CePtSi₂ for an extended low-temperature region. Inset: Details of resistivity around T_N under pressures up to 0.79 GPa (Nakano et al., 2009a).

in the inset (B) of Figure 116. These behaviors are consistent with the results of the resistivity measurement. The superconducting volume fraction of CePtSi₂ at 0.04 K is evaluated to be about 30%, indicating that the SC of CePtSi₂ should be an intrinsic phenomenon.



FIGURE 115 (A) Phase diagram of CePtSi₂ under pressure. The dashed line is the expected pressure dependence of $T_{\rm N}$. The dash-dotted line is a linear extrapolation of the pressure dependence of $T_{\rm N}$ based on the magnetic interactions model for a two-dimensional AFM. Pressure dependence of (B) T_1 , T_2 , and $T_{\rm max}$, (C) ρ_0 and *n*, respectively. The lines are guides to the eye (Nakano et al., 2009a).

The pressure dependence of the high-temperature resistivity is also interesting. As shown in Figure 114B, T_1 increases with increasing pressure up to 0.9 GPa, whereas T_2 decreases. The pressure dependence of T_1 and T_2 was reported for several Ce-based Kondo compounds, such as



FIGURE 116 Resistivity of CePtSi₂ with a magnetic field up to 0.7 T under 1.7 GPa. Inset: (A) Magnetic field dependence of T_c at 1.7 and 1.8 GPa evaluated from resistivity and ac susceptibility, respectively. Inset: (B) Temperature dependence of χ_{ac} for CePtSi₂ under 1.8 GPa in various magnetic fields (Nakano et al., 2009a).

CeCu₂Si₂ (Holmes et al., 2004), CeCu₂Ge₂ (Jaccard and Holmes, 2005), and CeAl₂ (Miyagawa et al., 2008), in which T_1 and T_2 are associated with modified Kondo temperatures owing to the CEF splitting. It should be noted that T_1 and T_2 merge into a single maximum (at T_{max}) above 1.15 GPa. We defined this pressure as P_v , which is nearly the same as P_{c1} . In general, the Kondo effect is enhanced by applying pressure because of the enhanced hybridization between the conduction d- and magnetic f-electrons due to the decrease in lattice constants and consequent overlap of CEF-split levels. Thus, the increases in T_1 and T_{max} indicate an increase in T_K . On the other hand, the decrease in T_2 may be attributed to CEF rather than the variation of T_K .

Low-temperature resistivity around the QCP is well represented by the relation, $\rho_m = \rho_0 + A'T^n$. Here, ρ_0 is the residual resistivity, A' is a constant and n is an exponent characteristic to the electronic and magnetic

state of the materials. The parameter n is close to 2, 5/3, 3/2, and 1 in a conventional FL, three-dimensional ferromagnet, three-dimensional antiferromagnet, and two-dimensional antiferromagnet, respectively (Moriya, 1985; Moriya et al., 1995).

Figure 115C displays ρ_0 and *n* for CePtSi₂ evaluated by fitting the present experimental data between 0.2 and 0.8 K to the above equation as a function of pressure. ρ_0 increases with pressure followed by a maximum around 1.2 GPa, indicating an enhancement of Kondo fluctuations. The value of *n* is 2 at ambient pressure, and it decreases with increasing pressure and becomes close to 1 around 1.2 GPa, suggesting that the AFM in CePtSi₂ has two-dimensional interactions rather than three-dimensional ones. Above 1.2 GPa, *n* increases and becomes 1.6 at 2.6 GPa, indicating the recovery of the FL state. The minimum of *n* and maximum of ρ_0 show that a QCP of the AF phase of CePtSi₂ exists around 1.2 GPa. The QCP is close to P_{c1} as shown in Figure 115A, and smaller than 2 GPa predicted from the initial slope of T_N versus pressure ($dT_N/dP = -0.9$ K GPa⁻¹). The pressure dependence of T_N is predicted as shown by the dashed line in Figure 115A.

According to the magnetic interactions model (Moriya, 1985), the magnetic ordering temperature T_N collapses owing to quantum fluctuations and is proportional to $|P - P_c|^x$, where x = 2/3 and 1 for a threeand two-dimensional antiferromagnet, respectively (Mathur et al., 1998; Millis, 1993). Indeed, T_N exhibits a linear decrease up to 0.79 GPa as shown in Figure 115A. Linear extrapolation of the pressure dependence of T_N , which is based on this model for the two-dimensional AF, is shown in Figure 115A as a dash-dotted line. That crosses the *P*-axis around P_{c2} , indicating that the AFM predicted by linear pressure dependence is suppressed by evolving the superconducting phase.

Note that the superconducting phase appears above P_{y_i} which is consistent with the QCP of the AF phase, as shown in Figure 115A and B. Similar type of SC is observed in CeCu₂(Ge, Si)₂ (Bellarbi et al., 1984; Jaccard et al., 1999; Thomas et al., 1996; Yuan et al., 2003), CeNiGe₃ (Nakashima et al., 2004), and Ce₂Ni₃Ge₅ (Nakashima et al., 2006), in which the superconducting phase appears around $P_{\rm v}$. Jaccard et al. (1999) reported that the merging of T_1 and T_2 indicates an entrance in an IV state of Ce, while T_K is of the order of the CEF splitting, and Holmes et al. have pointed the possibility of Ce-based SC due to valence fluctuations (Holmes et al., 2007). In CePtSi₂, the crossover from the CK state to an IV state is suggested from the change in the magnetoresistance (MR; Miyagawa et al., 2006) and resistivity (Oomi et al., 1994a) around $P_{\rm v}$. This IV state would further perturb the AF phase predicted by linear pressure dependence around the P_{v} . Judging from these results, we propose that the AF phase, collapsed by magnetic-nonmagnetic quantum fluctuations, is further suppressed by the valence fluctuations of Ce, and SC arises in CePtSi₂.

In summary, the superconducting phase with the maximum T_c of 0.14 K at 1.7 GPa is induced by applying pressure between 1.4 and 2.4 GPa in the AFM Kondo compound CePtSi₂. The AFM is suppressed and disappears above 1 GPa, and the FL like T^2 dependence in ρ recovers with increasing pressure. T_1 and T_2 , the modified Kondo temperatures, merge into a single T_{max} around 1.2 GPa which is consistent with the QCP. These experimental results suggest that the SC in CePtSi₂ is induced owing to quantum instability of possible two-dimensional AF phase and valence fluctuations of Ce.

4.2.3 UGe₂

UGe₂ is a ferromagnet with $T_{\rm C} = 52$ K. Figure 117 shows the magnetization and inverse magnetic susceptibility for a single crystal at ambient pressure along the easy magnetization axis in an applied field of 0.1 T. Right inset shows a typical hysteresis loop at 4.5 K along the easy axis. UGe₂ crystallizes in the orthorhombic structure with lattice parameters a = 4.09, b = 15.20, and c = 3.96 Å (Onuki et al., 1992). Left inset of Figure 117 shows the orthorhombic unit cell. It has been reported that the physical properties of UGe₂ show a large anisotropy reflecting the crystal structure (Onuki et al., 1992; Oomi et al., 1993c). There have been many investigations because the compound shows anomalous properties under high pressure.



FIGURE 117 The magnetization and inverse magnetic susceptibility of UGe₂. Left inset represents the orthorhombic unit cell; right inset depicts a typical hysteresis loop at 4.5 K measured along the easy magnetization axis (Saxena et al., 2000).



FIGURE 118 Temperature dependence of the electrical resistivity ρ of UGe₂ measured along the *a*-axis at various pressures. The Curie temperature T_c and the phase transition temperature T_x at ambient pressure are shown in the inset (Oomi et al., 1998).

Figure 118 shows an example of the electrical resistivity ρ along the *a*axis (I//a) at various pressures as a function of temperature. ρ at ambient pressure shows a smooth decrease with decreasing temperature and then a sudden decrease is observed near 52 K, which corresponds to the ferromagnetic ordering. The inset in Figure 118 shows the value of $d\rho/$ dT as a function of T at ambient pressure. There are two peaks in the temperature dependence of $d\rho/dT$, a sharp peak due to the ferromagnetic ordering and a broad peak which may correspond to a magnetic phase transition, the origin of which was discussed in Section 2.2.2. The Curie temperature $T_{\rm C}$ is defined as the temperature of the half value of $(d\rho/$ dT)_{peak} – $(d\rho/dT)$ _{para}, which is shown by an arrow in the inset. The transition temperature T_x corresponding to the broad peak is determined as the temperature where $d\rho/dT$ begins to decrease with decreasing temperature, which is also shown in the inset. An anomaly near T_x was observed in the thermal expansion coefficient, the Hall coefficient, and the thermoelectric power (Nishimura et al., 1994; Ōnuki et al., 1992; Oomi et al., 1993c). The ferromagnetism of UGe₂ seems to be complex because the ρ -*T* curve along the *b*-axis shows a hump below T_C which is reminiscent of AFM with a gap (\overline{Onuki} et al., 1992). Both T_C and T_x decrease upon applying pressure with coefficients $\partial T_{\rm C}/\partial P = -14$ K/GPa and $\partial T_{\rm x}/\partial P =$ -23 K/GPa, respectively. The anomaly at $T_{\rm C}$ in the ρ -T curve due to ferromagnetic ordering disappears above 1.5 GPa.

Figure 119 shows the temperature dependence of the linear thermal expansion $(\Delta l/l)_a$, $(\Delta l/l)_b$, and $(\Delta l/l)_c$ along the *a*-, *b*-, and *c*-axes at ambient



FIGURE 119 Temperature dependence of linear thermal expansion $(\Delta l/l)_a, (\Delta l/l)_b$, and $(\Delta l/l)_c$ of single-crystal UGe₂ at ambient pressure. The Curie temperature T_C is shown by an arrow (Nishimura et al., 1994).

pressure. $(\Delta l/l)_c$ decreases gradually with decreasing temperature, but it begins to increase around 50 K (T_c). The anomalous increase is due to the ferromagnetic order. Below T_c , a small knee is observed around 25 K, which was also observed in the temperature dependence of thermoelectric power and electrical resistivity as shown in Figure 118 (Ōnuki et al., 1992). The temperature dependence of $(\Delta l/l)_b$ is almost the same as that of $(\Delta l/l)_c$, except for a broad maximum around 30 K. In the case of *a*-axis, the behavior is different from those of the *b*- and *c*-axes below T_c , reflecting the orthorhombic crystal structure. Below 50 K, $(\Delta l/l)_a$ decreases with decreasing temperature.

Figure 120 depicts the linear thermal expansion along *a*- and *b*-axes at high pressure. $(\Delta l/l)_a$ shows a smooth decrease with decreasing temperature and then a sudden decrease is observed near T_C , while $(\Delta l/l)_b$ begins to increase below T_C . Below 1.5 GPa, the spontaneous MS is clearly observed. The linear thermal expansion coefficient α_b at ambient pressure is shown in the inset of Fig. 120B. An anomaly was observed near T_x , which also decreases as pressure increases. This result is consistent with the result of the electrical resistivity (Oomi et al., 1998). The anomaly due to ferromagnetic ordering becomes less prominent with increasing pressure, and T_C also decreases.

To examine the temperature dependence of volume change, the fractional change $\Delta V/V$ in volume was calculated as a function of temperature from the following relation:

$$\Delta V/V = (\Delta l/l)_a + (\Delta l/l)_b + (\Delta l/l)_c.$$
(37)



FIGURE 120 Linear thermal expansion $(\Delta l \land l)$ of single-crystal UGe₂ along the *a*- and *b*-axes as a function of temperature at various pressures. The Curie temperature T_{C} is shown by an arrow (Nishimura et al., 1994; Oomi et al., 2001).

The above relation is easily derived by using V = abc. The coefficients of volume thermal expansion α_V are obtained by differentiating $\Delta V/V$ with respect to *T*. Figure 121 indicates α_V at various pressures below 80 K. α_V decreases discontinuously at T_C , which is shown by arrows in this figure. T_x is also clearly seen in the α_V curve.



FIGURE 121 Thermal expansion coefficient α_V of single-crystal UGe₂ under pressure. T_x and T_c are shown by arrows (Oomi et al., 2002).

It is well known that the magnetic contribution to the temperature derivative of the electrical resistivity $d\rho/dT$ should be proportional to the magnetic part of the specific heat C, $d\rho/dT \propto C$ (Richard and Geldart, 1973). Further, the Grüneisen relation is described as Eq. (21). Since κ , V, and Γ are weakly dependent on temperature, one can consider α to be roughly proportional to C. Then α_c is also proportional to $d\rho/dT$. Figure 122 shows the temperature dependence of α_a and $d\rho/dT$. By applying pressure, $T_{\rm C}$ decreases and the width of the peak due to ferromagnetic ordering becomes broader. It should be noted that the shape of $d\rho/dT$ at 1 GPa is significantly different from that at the ambient pressure, but in the case of *c*-axis, the difference is not as strong. This suggests that the conduction electrons are scattered in a complicated way below $T_{\rm C}$. The paramagnetic state is induced at 2 GPa, and there are no clear peaks in the temperature dependence of α_a and ρ except a broad peak centered near 27 K in the ρ -*T* curve. Such a similarity has been reported for other rare earth compounds (Okita, 1991).

In order to examine the T^2 dependence in the ρ -T curve due to spin fluctuation and spin wave excitation in the range $T \ll T_C$, we plotted ρ at low temperature as a function of T^2 , which is shown in Figure 123. A T^2 dependence is seen in this plot. The range showing a T^2 dependence depends on the pressure. It is easily seen that the slope of the plot is large near the critical boundary of ferromagnetism. The values of A are shown in Figure 124 as a function of pressure. A is found to increase with pressure below 1 GPa followed by a decrease above 1.5 GPa. The magnitude of A is known to be proportional to $1/T_0^2$ (Thompson and Lawrence, 1994), where T_0 is a characteristic spin fluctuation temperature, that is,



FIGURE 122 Temperature dependence of (A) the thermal expansion coefficient α_a and (B) the temperature derivative of ρ of single-crystal UGe₂ at high pressure (Oomi et al., 1998).

 $T_0 \propto 1/\sqrt{A}$. The pressure dependence of $1/\sqrt{A}$ is shown in the inset of Figure 124. \sqrt{A} or T_0 is extrapolated to 0 around 1.3 GPa. In other words, *A* shows a divergence at a critical pressure $P_x \sim 1.3$ GPa.

In a narrow range of pressures below $P_x \sim 1.3$ GPa, and thus within the ferromagnetic state, SC has been reported to appear in the ferromagnetic regime (Huxley et al., 2001; Saxena et al., 2000). Figure 125 shows the resistivity of UGe₂ near P_x where the value of A shows a divergence. A sudden and complete loss of resistivity appears in the millikelvin temperature range below T_c . This plot of resistivity against the square of the temperature is roughly consistent with the form $\rho(T) = \rho_0 + AT^2$. The lower inset illustrates the typical pressure dependence of A around P_{cr} and the upper inset gives an example of the variation of the



FIGURE 123 ρ of single-crystal UGe₂ at low temperature. The solid lines show the T^2 dependence (Oomi et al., 1998).



FIGURE 124 The coefficient of the T^2 term of single-crystal UGe₂ as a function of pressure. The solid and dashed curves are guides to the eye. The pressure dependence of the value of $1/\sqrt{A}$, which corresponds to the characteristic energy, is plotted in the inset (Oomi et al., 1998).



FIGURE 125 The resistivity of UGe₂ at approximately 1.4 GPa. The lower inset illustrates the typical pressure dependence of A around P_x , and the upper inset gives an example of the variation of the superconducting transition temperature with external magnetic field (Saxena et al., 2000).

superconducting transition temperature with external magnetic field, which is consistent with the result of Oomi et al. (1998) as shown in Figure 124. The quadratic coefficient *A* has a very pronounced pressure dependence and rises rapidly at a pressure $P_x \sim 1.3$ GPa close to (but distinctly below) P_c and within the narrow pressure window where SC is indeed observed, that is, the quasiparticle interactions and thus *A* is expected to be largest at the critical boundary separating ferromagnetism and paramagnetism; namely, at P_c largest than at the lower pressure P_x . There is, however, evidence for the existence of a crossover anomaly within the ferromagnetic state whose characteristic temperature T_x collapses toward zero also near P_x .

The upper critical field H_{c2} is in excess of 3 T near the maximum of T_c and is much higher than normally expected for conventional superconducting inclusions (Agarwal, 2000). Moreover, the apparent initial gradient H_{c2}/T near T_c is anomalously large and consistent with that expected in the presence of an internal field arising from ferromagnetic order.

The ac susceptibility below $T_{\rm C}$ also tends to the limit of -1 (in SI units), as expected in the presence of bulk SC. Figure 126 shows the typical form of the magnetic susceptibility near 1.3 GPa (Saxena et al., 2000).

The data for the pressure dependence of $T_{\rm C}$ and $T_{\rm x}$ have been summarized in Figure 25B in Section 2.2.2. It is very interesting to note that $T_{\rm x}$ disappears near the pressure dependence where $T_{\rm c}$ shows the maximum (Huxley et al., 2001; Saxena et al., 2000). Thus the phase transition at $T_{\rm x}$ is closely related with the occurrence of SC.



FIGURE 126 The ac magnetic susceptibility of UGe₂ near 1.3 GPa (Saxena et al., 2000).

It seems to be important to clarify the electronic properties of UGe₂ in the wide range of pressure and temperature in order to explore the origins and mechanisms of SC in UGe₂. Figure 127A indicates the values of ρ_a at fixed temperatures, T = 4.2 and 10 K (below $T_{\rm C}$), as a function of pressure (Oomi et al., 2003). A peak in the pressure dependence of ρ_a is found around 1 GPa, which suggests a large electronic and magnetic fluctuation near 1 GPa and may correspond to some kind of phase transition (Oomi et al., 2000, 2002). The details of this phase are not known at present, but it is well established that this phase is closely related to the occurrence of pressure-induced SC. Figure 127B shows the ρ_a above T_C as a function of pressure. There are some anomalies in the pressure dependence of ρ_a . For example, ρ_a at 100 K decreases with pressure almost in a linear fashion up to 1 GPa, but the rate of decrease becomes slow above 1 GPa. This phenomenon is also observed at 150 K, but the anomalous behavior is less prominent than that at 100 K. On the other hand, ρ_a above 200 K is found to show a smooth decrease with pressure and no anomalous pressure dependence is found above 200 K.

Thermal expansion of UGe₂ also shows anomalous temperature dependence, in which the length of each axis shows anomalous expansion or shrinkage (Nishimura et al., 1994; Oomi et al., 1993c). In order to make clear the pressure dependence of thermal expansion coefficients, we show the thermal expansion coefficients along the *a*-axis, $\Delta \alpha_a(T,P) = \alpha_a(T,P) - \alpha_a(T,0)$, as a function of pressure at 20 K (below T_C) and 80 K (above T_C) in Figure 128. $\Delta \alpha_a$ at 20 K increases with pressure and shows a peak around 1.5 GPa, which corresponds to the ferromagnetic–paramagnetic transition (Oomi et al., 2002). On the other hand, $\Delta \alpha_a$ at 80 K is found to show similar peak around 1.2 GPa, although it is in the paramagnetic phase. The height



FIGURE 127 Pressure dependence of the electrical resistivity, (A) below and (B) above T_C (Oomi et al., 2003).

of peak in the paramagnetic phase is lower than that at 20 K (in FM phase). This finding is also very surprising because the magnetic state below 50 K is different from that above 50 K. This fact implies that the phase above 80 K may be not a "'pure'" paramagnetic phase but some kind of mixed phase including magnetic impurities or magnetic clusters such as superparamagnetic phase. Nishioka et al. (2002) suggested that the hpp at low temperature is regarded as an inhomogeneous phase containing very small magnetic domains. This result seems to be consistent with the above-mentioned result.

From the pressure dependence of volume (Oomi et al., 2002), the isothermal compressibility κ_V was calculated at various temperatures. The result is shown in Figure 129 as a function of temperature. The value of κ_V increases with decreasing temperature and the point at 10 K is higher than that extrapolated from high-temperature range. This temperature



FIGURE 128 Thermal expansion coefficient of UGe₂ along *a*-axis below and above T_c , where $\Delta \alpha_a(T,P) = \alpha_a(T,P) - \alpha_a(T,0)$ (Oomi et al., 2003).



FIGURE 129 Temperature dependence of the compressibility of UGe₂ (Oomi et al., 2003).

dependence is in sharp contrast to the normal metallic behavior, in which κ_V decreases with temperatures, that is, materials should become hard at low temperature. The softening below T_C is explained by a large magnetovolume effect, in which the volume is expanded by magnetic ordering (Nishimura et al., 1994; Oomi et al., 1993c). This result is considered to be due to magnetic and structural inhomogeneities in the paramagnetic phase of UGe₂, which may give rise to a large compressibility. This fact also supports the consideration in the foregoing paragraph.

Figure 130 summarizes the present data as an extended P-T phase diagram of UGe₂. This diagram includes the ferromagnetic phase, a kind of density wave phase, and the well-known pressure-induced



FIGURE 130 The extended P-T phase diagram of UGe₂ derived from the data discussed in Section 4.2.3 (Oomi et al., 2003).

superconducting phase (see Figure 25B in Section 2.2.2). It should be noted that the boundary in the inhomogeneous phase coincides with the peak (1.1–1.2 GPa) where T_c shows a maximum. It suggests that there may be an inhomogeneous phase above T_c , in which some persistent magnetic domains or clusters (like in a superparamagnetic phase or crystallographically disordered phase) may exist. These inhomogeneities result in unstable magnetic and electronic states to give an anomalous pressure dependence of the electrical resistivity, thermal expansion, and the anomalous temperature dependence of compressibility.

5. NEW PHENOMENA UNDER HIGH PRESSURE

In this chapter, we introduce recent topics related to novel pressureinduced electronic states observed in rare earth compounds. We show first the anomalous pressure-induced magnetic order which appears by applying uniaxial pressure in Ce and Yb compounds. Recent progress in this research field will be described. The second topic is amorphous alloys including Ce and difference of electronic properties between crystalline and amorphous states. The third topic is magnetic multilayers including rare earth elements in which large MR is observed. The details of the pressure effect on the magnitude of MR are introduced and discussed by comparing with the results obtained in Fe/Cr magnetic multilayers, in which large enhancement of MR at high pressure was reported.

5.1 Pressure-induced magnetic order

5.1.1 CeNiSn

The Kondo semimetal CeNiSn, which has the orthorhombic *ɛ*-TiNiSi-type crystal structure (space group *Pnma*), has lattice constant a = 7.54 Å, b = 4.60 Å, c = 7.61 Å) and it forms a pseudogap in the DOSs at the Fermi level (Takabatake et al., 1990). Hydrostatic pressure measurements have been done by many authors (Hiraoka et al., 1994; Kurisu et al., 1988; Uwatoko et al., 1992a). The pseudogap in CeNiSn is strongly suppressed by the increase of the degree of hybridization. The carrier concentration increases together with the recovery of the DOSs at the Fermi level. Further, suppression of antiferromagnetic correlations upon applying pressure was deduced from a neutron inelastic-scattering experiment (Sato et al., 1996).

It is interesting to compare the effect of pressure with that of uniaxial pressure. Unlike under uniaxial pressure, CeNiSn exhibits a transition from a pseudogapped state to a magnetically ordered state for *P*//*b*-axis and *P*//*c*-axis, while no transition occurs under *P*//*a*-axis. The magnetic susceptibility χ at various uniaxial pressures is shown in Figure 131. At ambient pressure, the temperature dependence of the susceptibility



FIGURE 131 χ plotted versus temperature at various pressures applied to a single crystal of CeNiSn along (A) *a*- and (B) *c*-axes. Solid line represents earlier data (Umeo et al., 1999).

is identical to previous results (Takabatake et al., 1996). For P//H//a, the susceptibility decreases with increasing pressure P, whereas the maximum temperature at 13 K hardly changes. But, for P//H//c, ξ is strongly increased with development of a pronounced maximum at 3.7 K above 0.25 GPa. This maximum of χ may be associated with the occurrence of antiferromagnetic order.

To clarify the origin of maximum in χ , the specific heat *C* has been measured under pressure up to 0.37 GPa. The temperature dependencies of *C* of CeNiSn at several pressures parallel to the *a*-, *b*-, and *c*-axes are shown in Figure 132. For *P*//a-axis, the value of *C* decreases slightly with pressure in the temperature range of the measurements. By contrast, for *P*//*b*-axis and *P*//*c*-axis, *C* increases with pressure and shows a maximum around 3.7 K at 0.25 and 0.13 GPa, respectively. With further increase in pressure, another peak appears around 3 K.

The C_{el}/T for selected pressures is shown in Figure 133. For P//c-axis = 0.16 GPa, the coexistence of the maximum around 6 K with the peak at 3 K implies that the AF state evolves from the state where the pseudogap remains. As is shown by the solid curves, the temperature variations of C_{el}/T in the nonordered state could be reproduced by the use of the V-shaped DOS (see inset of Figure 133) with a finite value at the Fermi level (Nishigori et al., 1996; Takabatake et al., 1998).

The peak of both *C* and χ clearly indicates that AFM order sets in. This is consistent with the T^3 dependence of *C* below 2.5 K for *P*//*c*-axis, which can be regarded as characteristic of the excitation of AFM magnons.

The dependence of the AF transition temperature T_N on the applied pressure for P//c is shown in Figure 134. The most significant feature is that once T_N appears at 4 K above 0.1 GPa, it does not change with further increase in P. This fact indicates the pressure-induced transition to be a first-order transition.

CeNiSn undergoes a transition from a pseudogapped state to a magnetically ordered state under uniaxial pressure for P//b-axis and P//caxis, while no transition occurs under P//a-axis. Since the critical pressure for this transition is as small as 0.1 GPa, CeNiSn should be located in the vicinity of the QCP. As to the microscopic origin of the anisotropic response, the local symmetry of Ce ions in this compound is quasitrigonal when viewed along the a direction (Higashi et al., 1993). This trigonal symmetry is thought to be a prerequisite for the formation of the pseudogap in the renormalized band which is originated from the anisotropic c-f hybridization (Ikeda and Miyake, 1996; Kagan et al., 1997). Here, cmeans the conduction electrons. When a uniaxial pressure is applied along the b- and c-axes, the trigonal symmetry would be lowered, while it is maintained for P//a-axis. The loss of the quasitrigonal symmetry may be responsible for the pressure-induced magnetic transition. Another scenario is that the elongation along the a-axis under P//b-axis CeNiSn

O 0 GPa

□ 0.25 ▼ 0.13

00

1.0

0.5

0

1.0





FIGURE 132 Specific heat C of CeNiSn as a function of T under uniaxial pressure (Umeo et al., 1999).

and P//c-axis may weaken the c-f hybridization and thus brings the system to the magnetically ordered state, as is expected from Doniach's phase diagram (Doniach, 1977; Iglesias et al., 1997).



FIGURE 133 Temperature dependence of the electronic specific heat C_{el} divided by temperature. Solid lines are the fits with a V-shaped density of states depicted in the inset. (Umeo et al., 1999).



FIGURE 134 Pressure dependence of T_N of CeNiSn (Umeo et al., 1999).

5.1.2 YbInCu₄

Yb compounds, which are a counterpart of Ce compounds, are known to show numerous anomalies of physical properties under high pressure (Mignot and Wittig, 1981; Nowik et al., 1988; Umeo et al., 2007; Winkelmann et al., 1998). The response of the physical properties of Yb

compounds to applied pressure is in sharp contrast to that of Ce compounds. For example, the temperature of the resistance maximum T_{max} which roughly corresponds to the Kondo temperature T_{K} , increases with pressure for almost all Ce compounds (Kagayama and Oomi, 1993b), but it decreases for Yb compounds. In some Yb compounds, the CK state is induced by applying pressure as in YbAgCu₄ (Graf et al., 1995) and YbCo₂Zn₂₀ (Matsubayashi et al., 2010b; Saiga et al., 2008). The intermetallic compound YbInCu₄, which crystallizes in the AuBe₅ type (C15b) structure with the lattice constant, a = 7.156 Å (Felner et al., 1987; Kojima et al., 1990), is one of the interesting Yb compounds. The most interesting feature of YbInCu₄ is that it shows a valence transition from a high-temperature stable trivalent Yb³⁺ to a low-temperature mixedvalence Yb around 50 K ($=T_v$). T_v is found to be strongly dependent on pressure with $dT_v/dP \sim -20$ K/GPa (Kojima et al., 1988). Nowik et al. (1988) reported an anomaly near 0.6 GPa in the pressure dependence of $T_{\rm v}$. However, no anomaly in the $T_{\rm v}$ -P curve was observed by Kojima et al. (1988) and Matsumoto et al. (1992). In this section, we discuss the effect of pressure on the valence transition of YbInCu₄ by measuring bulk modulus, magnetization, and electrical resistivity up to 13 GPa.

Figure 135 shows the relative change in the lattice constant a/a_0 as a function of pressure at room temperature, where *a* and a_0 are the lattice constants at high and ambient pressure, respectively. Since there are no new Bragg peaks up to 13 GPa, the AuBe₅ structure is stable at room temperature at least to 13 GPa. A discontinuous change in the value of a/a_0 , to be caused by the γ - α transition in Ce metal (Franceschi and Olcese, 1969), is not observed in the present pressure range within experimental error. This result indicates that a discontinuous valence transition as observed at T_v is not induced by pressure up to 13 GPa at room



FIGURE 135 Pressure dependence of the relative change of lattice parameter a/a_0 of YblnCu₄ at room temperature (Oomi et al., 1994b).

temperature. In order to estimate the bulk modulus, we attempted a leastsquares fit of the data in Figure 135 to the Murnaghan's equation (1) (see the solid curve in Figure 135). The values of B_0 and B_0' were found to be $B_0 = (112 \pm 2)$ GPa and $B_0' = 4.0 \pm 0.2$, respectively. B_0 of YbInCu₄ is slightly larger than that of the YbAgCu₄, 108 GPa (Bauer et al., 1993). The results obtained until now are summarized in Table 5 together with those of the related CK or HF compounds: YbAl₂ (Penney et al., 1982), YbAgCu₄ (Bauer et al., 1993), and CeInCu₂ (Kagayama et al., 1990) for comparison. The small value of B_0' indicates a relatively slow stiffening of the lattice with increasing pressure, which is similar to Ce compounds. This fact indicates that the electronic state of the compounds having unstable 4f electrons has a strong effect not only on the value of B_0 but also on B_0' . The small value of B_0' of YbAgCu₄ suggests a large change in the electronic state due to increasing hybridization by pressure (see Table 1 in Section 1). There seems to be a relationship between B_0 , the electronic specific heat coefficient γ , and the lattice constant a_0 .

The electronic state of YbInCu₄ changes from IV state to the CK state by substituting In for Ag (Yoshimura et al., 1990; Kojima et al., 1992). This is considered to be due to a decrease in the hybridization between the localized 4f electrons and the conduction band caused by the substitution of Ag. Since the application of pressure essentially results in an increase in the hybridization, the effect of Ag addition is opposite to that of pressure. Taking into account these facts and the pressure dependence of T_{y} , YbInCu₄ may correspond to a hpp or a kind of compressed state of YbAgCu₄ to have a larger bulk modulus than YbAgCu₄. This consideration explains gualitatively the above-mentioned values for the bulk modulus. Further, from the theoretical calculations (Lavagna et al., 1983), it was revealed that the bulk modulus in the Kondo state is always lower than that in the non-Kondo or normal state. If we consider that YbAgCu₄ is in the Kondo state and YbInCu₄ in the normal trivalent state, the bulk modulus of YblnCu₄ would be larger than that of YbAgCu₄. This is also consistent with the present results. On the other hand, for YbInCu₄,

nJ∕ B _o IK ²) (GPa)	<i>B</i> ₀ ′	T _{max} (K)	∂T _{max} ∕∂P (K∕GPa)
112	4.0	_	_
5 108	3.3	100	-14
54.7	19.7	275	-4.2
43.1	5.0	_	_
90	3.9	27	0.4
	$ \begin{array}{c c} nJ \neq & B_0 \\ (GPa) \\ \hline \\ 112 \\ 5 \\ 5 \\ 5 \\ 54.7 \\ 43.1 \\ 00 \\ 90 \end{array} $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

TABLE 5 Summary of the present results and data of some CK compounds

the effect of the electronic state on the lattice stiffening may be relatively small, which indicates that the Yb³⁺ state is stable up to 13 GPa. This result is consistent with that of the electrical resistivity in which the *P*–*T* curve of YbInCu₄ shows normal properties above T_v (Felner et al., 1987).

Electrical resistivity measurements of YbInCu₄ were performed under high pressure up to 7.0 GPa and temperature down to 0.3 K (Kurita et al., 2006). Figure 136A and B shows the temperature dependence of the electrical resistivity of YbInCu₄ at low temperature. The electrical resistivity of YbInCu₄ decreases with temperature almost linearly above valence transition temperature T_v and then drops abruptly at $T_{v'}$ as shown in Figure 136A. T_v decreases linearly with increasing pressure up to 1 GPa as shown in Figure 142. At ambient pressure, the resistivity



FIGURE 136 (A) Temperature dependence of the electrical resistivity of YbInCu₄ at low-temperature measured using piston cylinder cell (A) (Hedo et al., 2003) and diamond-anvil cell (B) (Kurita et al., 2006). Arrows indicate the temperature where there is a "knee" in $\rho(T)$ in (B).

above T_v increases rapidly due to a large internal strain of the sample, induced by thermal cycling through the transition. At high pressure, the resistivity does not change much after the transition has taken place.

YbInCu₄ exhibits large hysteresis below 3 GPa around T_v as shown in Figure 137. The resistivity at 2.9 GPa exhibits hysteresis near the valence transition temperature $T_v = 6.2$ K. For P = 3.39 GPa; the valence transition disappears, with no detectable hysteresis at low temperature. There is no observed hysteresis at the transition, and then the transition disappears above 3 GPa.

We tentatively fit the data obtained in previous and this work at low temperature to $\rho = \rho_0 + AT^2$. Both the residual resistivity ρ_0 and the resistivity coefficient *A* as a function of pressure show broad peaks around 3.5 GPa. And then, ρ_0 at low temperature is suppressed by increasing pressure from 3.3 to 5.5 GPa. This suggests that YbInCu₄ around 3.5 GPa may be in the vicinity of a QCP *P*_c, given the report of similar variations of *A* and is reported for pressure-induced superconductor CeCu₂Ge₂ (Jaccard et al., 1999), although pressure-induced changes in carrier density and ground-state degeneracy could provide an alternative interpretation (Figures 138 and 139).

Hedo et al. (2003) observed a "filamentary" SC (with a nonzero resistivity) above 0.74 GPa and below \sim 1.4 K, though it could not be detected



FIGURE 137 Electrical resistivity of YbInCu₄ versus temperature below 8 K at P = 2.94 and 3.39 GPa (Hedo et al., 2003).



FIGURE 138 Pressure dependence of the residual resistivity ρ_0 and coefficient A of YblnCu₄ in the relation $\rho = \rho_0 + AT^2$ (Kurita et al., 2006).



FIGURE 139 Low-temperature resistivity of YbInCu₄ in H = 0 and 0.05 T under P = 3.76 GPa. Solid line is *T*-linear line as guide to the eye (Hedo et al., 2003).

at ambient pressure, as shown in Figure 140. The drop of resistivity vanishes in magnetic field above 0.036 T. This SC survives up to 4 GPa and the superconducting temperature T_c is almost independent of the pressure. Above P_{cr} , the resistivity follows the linear behavior versus *T* in the range 0.9 to 2.5 K.

Figure 140 shows magnetization plotted versus temperature for a single crystal of YbInCu₄ at various pressures (Sarrao et al., 1998). At 1 bar, the temperature dependence of the susceptibility is identical to previous results (Sarrao et al., 1996), within experimental error. The sharp



FIGURE 140 Magnetic susceptibility of YbInCu₄ as a function of temperature at various fixed pressures (Sarrao et al., 1998).

rise at T = 40 K (P = 1 bar) due to the Yb valence change with increasing temperature decreases with increasing pressure at the rate of $dT_v/dP = -22.3$ K /GPa, which is slightly larger than previously reported (Immer et al., 1997). This difference may be caused mainly by variation of pressure inside the microcell with temperature. At high temperatures, the susceptibility follows the Curie–Weiss law, with values of the paramagnetic temperature and paramagnetic moments, $\theta_P = -7$ K and $\mu_{Yb} = 4.50$ (μ_B/Yb) at 1 bar. This Curie–Weiss behavior does not change under pressure within experimental error.

Mito et al. (2003) measured the temperature dependence of the magnetization at several pressures blow 3.5 K and up to 27 GPa as shown in Figure 141, where all the data were taken following zero-field-cooled heating protocol under H = 3 Oe. At 0.98 GPa, there is no sign of magnetic ordering in the range of measuring temperature. T_v drastically decreases with increasing pressure like in the previous report (Koyama et al., 2005; Mito et al., 2003). On the other hand, once T_M abruptly appears at P_c (around 3 GPa), T_M shows a very weak pressure dependence up to 27 GPa.

The resulting pressure dependence of the onset temperatures T_{M} , T_v (Mito et al., 2003; Koyama et al., 2005; Kurita et al., 2006), and T_c (Hedo et al., 2003) are summarized in the pressure–temperature (*P*–*T*) phase diagram in Figure 142. The valence phase transition temperature T_v decreases linearly at the rate of -19.5 K /GPa with increasing pressure up to 1.5 GPa. Many other groups have reported similar values for the pressure dependence of T_v . At above 1.0 GPa, however, T_v decreases more gradually and is suppressed below 1.5 K at 2.5 GPa (Hedo et al., 2003; Kurita et al., 2006; Sarrao et al., 1998; Uchida et al., 2002).



FIGURE 141 Temperature dependence of magnetization of YblnCu₄ at various pressures (Mito et al., 2007).



FIGURE 142 Pressure dependence of T_{M} , T_{v} , and T_{c} of YbInCu₄.

The transition between the two low-temperature phases, the mixedvalence and the magnetically ordered phases, is of first order with respect to pressure. This implies that there is no QCP in the *P*–*T* phase diagram for YbInCu₄, as suggested from previous high-pressure nuclear quadrupole resonance (NQR) studies (Koyama et al., 2005; Young et al., 2005). The NQR measurements indicate that the whole phase boundary between the low-temperature mixed-valence state and the adjacent phases is of first order, and the magnetic ordering for $P > P_c$ is of second order. From these experimental results, it is concluded that YbInCu₄ above P_{cV} is in the vicinity of the QCP (Miyake and Narikiyo, 2002). Contrary to Ce-based systems, the HF state becomes robust with pressure increase in this Ybbased system. Therefore, the enhancement of the coefficient *A* and the residual resistivity ρ_0 in YbInCu₄ under pressure corresponds to a rapid decrease of those quantities observed in CeCu₂Ge₂ with the increasing pressure (Jaccard et al., 1999).

5.2 Amorphous Ce alloys under high pressure

Various interesting properties of 4f-electron systems such as CK and HF compounds have been generally studied using crystalline materials, where there is also periodicity of 4f electrons. The formation of the Fermi surface from 4f-electron bands is essential to many, if not all of these cooperative properties. Therefore, such behaviors are not expected to occur in disordered alloys without translational symmetry where the 4f electrons have non-Bloch-type states. However, interesting behaviors have recently been observed in Ce-based structurally disordered materials. Here, we introduce amorphous CeRu system as a typical example. Crystalline CeRu₂ compound is one of the famous itinerant 4f-electron materials to show SC ($T_c = 6.3 \text{ K}$, $\gamma = 27 \text{ mJ/mol K}^2$) (Hedo et al., 1998; Matthias et al., 1958). On the other hand, amorphous *a*-CeRu also shows HF-like behavior in the Ce-rich side and SC in the Ru-rich side (Homma et al., 1997).

The electrical resistivity as a function of temperature for a-Ce_xRu_{100-x} alloys is shown in Figure 143A. For x < 40, the superconducting transition is observed. Both the Ce₈₀Ru₂₀ and Ce₄₇Ru₅₃ samples have no superconducting transition down to 1.8 K, and instead, the ρ -T curves here show $\rho \sim AT^2$ dependence at the low-temperature region. Ce₈₀Ru₂₀ has a large A value of $1.54 \times 10^{-1} \ \mu\Omega \ cm/K^2$, which is about one order of magnitude larger than that of crystalline CeRu₂. Even in Ce₄₇Ru₅₃, the A value (= $4.3 \times 10^{-2} \ \mu\Omega \ cm/K^2$) is larger than that of CeRu₂. The A value for x = 67 was found to be one order of magnitude smaller than for x = 80. The $\rho \sim AT^2$ dependence of these alloys indicates that coherent Kondo state is probably formed at the low-temperature region.

Figure 143B shows C_p/T as a function of T^2 for a-Ce_xRu_{100-x} (x = 15, 47, and 80) at low temperature. C_p/T nicely follows a function of $\gamma + BT^2$ down to 8 K. C_p/T for x = 16, 23, 39, and 67 also follows the same behavior (not shown).



FIGURE 143 (A) Electrical resistivity versus log *T* for several *a*-Ce_xRu_{100-x} alloys (Obi et al., 2006), (B) C_p/T versus T^2 plots at low temperature for x = 15, 47, and 80. Dotted lines show $C_p/T = \gamma + \beta T^2$ relation (Amakai et al., 2007).

The Kadowaki-Woods (KW) plot (1986) of *A* and γ of *a*-CeRu alloys in the HF state (x = 67 and 80) is shown in Figure 144. In this figure, the solid line shows $A/\gamma^2 = 1.0 \times 10^{-5} \ \mu\Omega \ \text{cm}(\text{mol } \text{K}^2/\text{mJ})^2$, which is the KW relation followed by typical HF compounds. The dotted line shows $A/\gamma^2 = 0.7 \times 10^{-5} \ \mu\Omega \ \text{cm}(\text{mol } \text{K}^2/\text{mJ})^2$, which is the generalized KW relation $A/\gamma^2 = 1.0 \times 10^{-5}/(N(N-1)/2)$ (Kontani, 2004; Tsujii et al., 2005) with the full orbital degeneracy of N = 6 for Ce. The ratio of A/γ^2 for the present alloys shows almost the same value $0.5 \times 10^{-6} \ \mu\Omega \ \text{cm}$ (Ce mol K²/mJ)², and this is located between the full line and dotted line. Structurally disordered alloys such as a present system might give rise to



FIGURE 144 Log A versus log γ plots (KW plot) for *a*-CeRu with x = 67 and 80. Black filled circles indicate the value for amorphous alloys. Open squares indicate the values found in some crystalline Ce- and U-based HF compounds. The solid line is the KW relation and the dotted line is the generalized KW relation with N = 6 (Amakai et al., 2006, 2009).

increase of the high-symmetrical crystalline field by random arrangement of atoms. A recent study of *a*-CeMn alloys suggests an evidence of the HF from the large *A* and γ values with KW plot, where the effect of the orbital degeneracy has been pointed out (Amakai et al., 2006, 2009).

Effect of pressure for *a*-Ce₅₈Ru₄₂ was studied by Sakai et al. (1996). Figure 145A shows the resistivity of *a*-Ce₅₈Ru₄₂ at pressures up to 14 GPa. At ambient pressure, the resistivity of *a*-Ce₅₈Ru₄₂ increases with decreasing temperature and exhibits a broad maximum around 32 K. This behavior is roughly consistent with that of *a*-Ce₅₃Ru₄₇ in Figure 143. The resistivity decreases below 32 K probably due to the development of a coherent state of the 4f electrons. Above 60 K, the resistivity shows



FIGURE 145 Pressure dependence of resistivity of a-Ce₅₈Ru₄₂ shown using (A) linear scale and (B) logarithmic scale (Sakai et al., 1996).

Kondo-like log *T* dependence. As the pressure increases, the maximum shifts to the lower temperature with -4.4 K /GPa, indicating the decrease of T_{K} . The residual resistivity ρ_0 is reduced strongly with $d\rho_0/dP = -27 \,\mu\Omega \,\text{cm/GPa}$, which is larger than that of typical HF compounds such as CeCu₆ (Oomi et al., 1993b) and CeAl₃ (Kagayama et al., 1994e). The large decrease of ρ_0 is explained in terms of the reduction of the scattering of conduction electrons due to disordered magnetic moment, which is suppressed by delocalization of 4f electrons at high pressure.

The log *T* dependence is clearly seen up to 14 GPa as shown in Figure 145B. Deviation from the log *T* dependence is observed above 200 K at 0 and 2.1 GPa. This may be due to the phonon contribution which becomes dominant at high temperature. Since the slope of the straight line in Figure 145B decreases rapidly with increasing pressure, the contribution from Kondo scattering to the resistivity is suppressed by applying pressure. Figure 146 shows a value of m/m_0 as a function of pressure, where $m (= -\partial \rho / \partial \log T)$ and m_0 as a function of pressure are the values at high and ambient pressure, respectively. *m* decreases rapidly below 1 GPa and saturates above 10 GPa. *m* is related to the value of $JD(\varepsilon_F)$ as follows:

$$m = \frac{\partial \rho}{\partial \log T} \propto |JD(\varepsilon_{\rm F})|^3, \tag{38}$$



FIGURE 146 The relative change of the value of $m(=-\partial \rho / \partial \log T)$ of *a*-Ce₅₈Ru₄₂ as a function of pressure (Sakai et al., 1996).

where *J* is the exchange interaction between the conduction electrons and the localized 4f electron spins. $D(\varepsilon_{\rm F})$ is the DOSs at the Fermi level. According to this relation, the marked decrease of *m* with increasing pressure indicates that the $|JD(\varepsilon_{\rm F})|$ is decreased markedly by applying pressure. Since the value of *m* at 14 GPa is smaller than that at ambient pressure by an order of magnitude, $|JND(\varepsilon_{\rm F})|$ at 14 GPa is evaluated to be about half the value at ambient pressure.

In dilute Kondo systems, the $T_{\rm K}$ is related to $|JD(\varepsilon_{\rm F})|$ as follows:

$$T_K \propto \left(-\frac{1}{|JD(\varepsilon_{\rm F})|}\right).$$
 (39)

As mentioned above, the $|JD(\varepsilon_F)|$ decreases by application of pressure. This leads to a decrease in T_K according to the equation. $D(\varepsilon_F)$ is expected to decrease and |J| to increase with increasing pressure because the hybridization of the conduction electrons and 4f electrons increases at high pressure. The decrease in $|JD(\varepsilon_F)|$ in *a*-CeRu implies that the pressure dependence of |J| is weaker than that $D(\varepsilon_F)$. This result is in sharp contrast to crystalline HF compounds such as CeAl₃, in which the $J|D(\varepsilon_F)|$ increases with pressure.

Amorphous *a*-CeCu₆ was also studied under pressure by Kagayama et al., (1994a). Figure 147A shows the temperature dependence of r = R(T)/R(T = 200 K). At 0 GPa, *r* increases gradually with decreasing temperature and increases remarkably below 25 K. This is quite different from the crystalline sample *c*-CeCu₆ (Kagayama et al., 1994a). Below 20 K, *r* shows a linear relationship between *r* and log *T* as shown in Figure 147B, which identifies the Kondo scattering. It is clearly seen even at high pressure. The slope in the *r* versus log *T* plot increases drastically with increasing pressure. *m* of Eq. (38) for *a*- and *c*-CeCu₆ was also evaluated as



FIGURE 147 (A) The normalized resistance r = R(T)/R(T = 200 K) of *a*-CeCu₆ as a function of temperature at various pressure. (B) The temperature dependence of *r* below 20 K on the logarithmic scale of temperature. The straight line shows the liner part in the *r* versus log *T* plot (Kagayama et al., 1994a).

shown in Figure 148. They increase with increasing pressure which is in contrast to the case for *a*-Ce₅₈Ru₄₂ in Figure 146. The origin of these discrepancies is not clear at present. The values of $d(m/m_0)/dP$ are evaluated to be 4×10^{-4} and 1×10^{-2} GPa⁻¹ for *c*- and *a*-CeCu₆, respectively. The value of *a*-CeCu₆ is about 25 times larger than that of *c*-CeCu₆, which indicates that the Kondo effect in *a*-CeCu₆ is enhanced strongly by pressure.

In summary, a-Ce_xRu_{100-x} alloys (x = 67 and 80) exhibit HF-like behavior characterized by large γ and A. The ratios of A/γ^2 for those alloys show about $0.5 \times 10^{-6} \,\mu\Omega$ cm(Ce mol K²/mJ)² which is located in between the KW relation (full line) and generalized KW relation with N = 6(dotted line) as shown in Figure 144. By applying pressure, transport properties in a-Ce₅₈Ru₄₂ and a-CeCu₆ are drastically changed and T_K decreases in a-Ce₅₈Ru₄₂, but it increases in a-CeCu₆.

5.3 Negative MR of the magnetic multilayer Fe/Tb

The giant magnetoresistance (GMR) has been investigated extensively mainly for 3d transition metal systems not only from the viewpoint of applications but also to understand the fundamental transport properties



FIGURE 148 The value of the slope, $m(=-\partial \rho / \partial \log T)$, for *a*-CeCu₆ as a function of pressure. The pressure dependence of normalized values m/m_0 is plotted for *a*- and *c*-CeCu₆ (Kagayama et al., 1994a).

of metals and alloys. There have been a few reports for the pressure effect on the GMR. Recently, it has been reported that a large enhancement of GMR occurs in Fe/Cr magnetic multilayers (Suenaga et al., 2007), where the GMR is observed when the antiparallel arrangement of Fe layer spins changes to parallel one by applying magnetic field. This investigation sheds new light on the basic mechanism of the transport properties and GMR in Fe/Cr magnetic multilayers. Since only a few examples of such enhancements of GMR in magnetic multilayers have been reported until now (Sakai et al., 1998), it is worthwhile to explore such pressure-induced phenomena in novel magnetic systems.

Magnetic multilayer systems including heavy rare earth metals are known to have various magnetic properties, such as antiferromagnetic, spiral magnetic, or twisted magnetic structures. These magnetic structures can be realized in magnetic exchange spring multilayers. The magnetic exchange springs can tailor artificial domain walls. It has been argued that domain walls in a ferromagnet should give rise to MR (Levy and Zhang, 1997). Mibu et al. (1998) studied the effect of exchange springs in the SmCo/NiFe system. However, MR here is small (1.5%) and dominated by anisotropic magnetoresistance (AMR). Gordeev et al. (2001) demonstrated that the formation of short exchange springs in the YFe₂/TbFe₂ superlattice results in a large magnitude of MR, as high as 32%. In general, the directions of magnetization in consecutive layers can be switched when a magnetic field is applied, and MR changes dramatically as a whole.

The Fe/Tb multilayer system is expected to have some kind of twisted magnetic structure, caused by the competition among the exchange coupling, the Zeeman energy, and the anisotropy energy. Takanod et al. (2004) considered a twisting model where Fe magnetic moment and Tb magnetic moment make an angle with one another under the assumption that Fe magnetic moment is always aligned parallel to the magnetic field and that Tb magnetic moments are parallel coupled in the Tb layer. Figure 149 shows an *M*–*T* magnetic phase diagram of [Fe(12 nm)/Tb (15 nm)]₂₅ multilayer with long artificial period. In all regions, Fe magnetic moment is magnetically dominant. In the region "Fe-aligned," only Fe magnetic moments survive above 320 K which is the estimated Curie temperature of Tb in this multilayer. In the region "Ferri_L," Tb magnetic moment and Fe magnetic moment are ferrimagnetically coupled in the range *H* < *H*_C. This is due to the ordinary exchange coupling between Fe



FIGURE 149 Magnetic phase diagram of [Fe(12 nm)/Tb(15 nm)]₂₅ multilayer (Takanod et al., 2004).
and Tb magnetic moments, which is always negative. With increasing the magnetic field, twisted magnetic structure appears when the sample temperature is low, particularly below 150 K in this Fe/Tb multilayer, in the region "Twisted." This magnetic structure comes from the competition among the exchange coupling, the Zeeman energy, and the anisotropy energy. Further increase in the magnetic field beyond 1.5 T results in the "Ferro" phase where Fe and Tb magnetic moments are parallel to the magnetic field. "Ferri_{II}" phase appears in the middle range of temperature and the field exceeding the $H_{\rm C}$. The magnetic moments of the Tb layers depend upon the temperature, and they finally disappear at the boundary temperature 320 K. This magnetic phase generally comes from the condition that the total energy of the sample, which consists of the exchange coupling, the Zeeman energy, and the anisotropic energy, should be at the minimum. Computer simulations are necessary, taking into account these energies, to explain the magnetic phase diagram shown in Figure 149. The phenomenon of twisted state needed to be considered in detail that the magnitude and the direction of the magnetic moment of every atomic layer are estimated by molecular field from nearest neighbor interactions. Those magnitudes and directions can be different in each atomic layer. And it is also predicted that Tb magnetic moments have some spiral states, that is, the directions of Tb magnetic moments at the interface are opposite to the applied magnetic field and those inside of the Tb layer are aligned with the applied magnetic field.

Figure 150A shows the MR curve of Tb single layer at 4.2 K (Ohashi et al., 2008). Here, the magnitude of MR ratio is defined as

$$MR(H) = \frac{R(0) - R(H)}{R(0)}.$$
(40)

The slope dMR/dH is negative in the region of high magnetic field of up to 30 T, and no anomalies is observed in the MR(H) curve.

The magnitude of the negative MR ratio is MR(30 T) = 9.9%. Such a large MR of a heavy rare earth metal was reviewed by McGuire and Potter (1975), in which the giant magnitude of MR was obtained in Ho metal to be 32% at 4.2 K. Taking into account that Tb metal has very high magnetic anisotropy, the negative MR of Tb can also be due to an AMR effect. This suggestion is supported by the fact that the slope |dMR/dH| of Tb decreases slightly with increasing magnetic field. As shown in Figure 150A, the MR curve tends to saturate above 10 T but has a long tail at high magnetic field. As for the Fe/Tb multilayer, MR is symmetrical with respect the change of sign of the magnetic field $\pm H$, while the *M*–*H* curve shows a hysteresis loop (Takanod et al., 2004). Figure 150B shows the MR curve of [Fe(12 nm)/Tb(15 nm)]₂₅ at 4.2 K. Here, the giant negative MR is obtained to be *MR*(30 T) = 24.6%. Such a large negative MR has



FIGURE 150 The MR curves of (A) Tb at 4.2 K and (B) $[Fe(12 \text{ nm})/Tb(15 \text{ nm})]_{25}$ as a function of the magnetic field applied parallel to the plane. Inset shows the MR curve of Fe/Tb from -0.5 to 0.5 T (Ohashi et al., 2008).

never been reported in a multilayer system consisting of a transition metal and a rare earth metal. Moreover, it is found that MR is not saturated completely even at 30 T which is largely different from Fe/Cr case. Apparently, the MR of the Fe/Tb multilayer has been enhanced compared with that of the Tb monolayer film. Since the AMR effect is enhanced by spin polarization and spin–orbit interactions (Campbell et al., 1970), it is reasonable to assume that the AMR effects on the Tb layer is enhanced by spin polarization of the Fe layers.

At room temperature, *R* of $[Fe(12 \text{ nm})/Tb(15 \text{ nm})]_{25}$ multilayer is almost independent of pressure. The pressure coefficient $|R^{-1}\partial R/\partial P|$ is less than 1×10^{-3} GPa⁻¹, which is one order of magnitude smaller than those of Fe/Cr and Co/Cu multilayers (Oomi et al., 1997). Figure 151 shows the electrical resistance *R* of $[Fe(12 \text{ nm})/Tb(15 \text{ nm})]_{25}$ as a function of temperature at several pressures. At 0.1 GPa, *R* decreases with decreasing temperature, showing good linearity from room temperature down to ~220 K, but *R* deviates from linearity at low temperature. The slope



FIGURE 151 The electrical resistance of $[Fe(12 \text{ nm})/Tb(15 \text{ nm})]_{25}$ as a function of the temperature at several pressures (Ohashi et al., 2008).

 $\partial R/\partial T$ tends to increase with decreasing temperature slightly from \sim 220 K down to 50 K. It is caused by the ferromagnetic order of Tb at $T_{\rm C} \sim$ 219 K. Figure 152 shows a sharp change in the slope of the resistivity curve of metallic Tb at 229 K for a weak antiferromagnetic state and at 219 K for a ferromagnetic one (Ohashi et al., 2009).

R of Fe/Cr multilayer is almost independent of pressure above $T_{\rm C}$, indicating that the scattering process between conduction electrons and phonons is not changed by pressure up to 3.2 GPa. Below $T_{\rm C}$, on the other hand, we note a general increase in the total resistance of Tb with increasing pressure. It means that the spin-dependent scattering is enhanced with increasing pressure, since the ferromagnetic order of the Tb layer is suppressed. Indeed, the residual resistivity ratio R(280 K)/R(4.2 K) decreases with increasing pressure. The ratio R(280 K)/R(4.2 K) is obtained to be 1.28 at ambient pressure and that at 3.2 GPa is 1.26. This suggestion is consistent with the previous report that the spontaneous magnetization of Tb is suppressed by applying pressure (Bloch and Pauthenet, 1964). R-T curves show a minimum around $T_{\rm min} \sim 21$ K and a maximum around $T_{\rm max} \sim 4$ K, which is not observed in multilayers made from 3d transition metals such as Fe/Cr and Co/Cu (Oomi et al., 1997). Some of magnetic phase boundaries may exist near $T_{\rm max}$ and $T_{\rm min}$.



FIGURE 152 The electrical resistivity of Tb single layer as a function of the temperature. Inset shows temperature derivative of the resistivity (Ohashi et al., 2009).

but the reason is unknown in detail. Both T_{max} and T_{min} are independent of pressure.

Figure 153 shows MR ratios up to 8.5 T at 4.2 K at several pressures. It is already shown in Figure 150B that MR is not saturated completely even at 30 T. Further, the magnitude of MR decreases with increasing pressure. The effect of pressure on the magnitude of MR ratio, MR(8.5 T), is estimated by substituting H = 8.5 T in Eq. (40). Figure 154A shows the magnitude of MR ratio at 8.5 T, MR(8.5 T), as a function of pressure. MR (8.5 T) decreases proportionally to the applied pressure. The pressure coefficient is $(1/MR)d(MR)/dP \sim -0.025$ GPa⁻¹. In order to explain this result, we defined the magnitude of MR as $\Delta R = R(0) - R(8.5 T)$. By substituting ΔR into Eq. (40) at the magnetic field of 8.5 T, the MR ratio is obtained as MR(8.5 T) = $\Delta R/R(0)$. By differentiating the equation with respect to pressure, we obtain

$$\frac{1}{(\mathrm{MR})}\frac{\partial(\mathrm{MR})}{\partial P} = \frac{1}{\Delta R}\frac{\partial\Delta R}{\partial P} - \frac{1}{R(0)}\frac{\partial R(0)}{\partial P}.$$
(41)

It means that the effect of pressure on MR consists of two terms: one is the effect of pressure on ΔR and the other is that on R(0). As shown in



FIGURE 153 MR curve of $[Fe(12 \text{ nm})/Tb(15 \text{ nm})]_{25}$ at 4.2 K as a function of the magnetic field applied parallel on the plane. The value of MR is obtained by using Eq. (41) (Ohashi et al., 2008).

Figure 154B, R(0) at 4.2 K increases at the rate of $[1/R(0)][dR(0)/dP] = 6.0 \times 10^{-3} \text{ GPa}^{-1}$. Qualitatively, this result is consistent with the suggestion that the spin-dependent scattering is enhanced because of the suppression of the ferromagnetic order of the Tb layer. Indeed, as shown in Figure 151, the R(T) curve increases with increasing pressure below $T_{\rm C}$.

Further, as shown in Figure 154C, ΔR decreases at the rate of $(1/\Delta R)$ $(d\Delta R)/dP = -0.020$ GPa⁻¹ at 4.2 K. Since pressure suppresses the ferromagnetic order of the Tb layer, AMR effects can also be suppressed. Then ΔR decreases with increasing pressure. By substituting the values of [1/R(0)][dR(0)/dP] and $(1/\Delta R)(d\Delta R/dP)$ into Eq. (41), (1/MR) (dMR/dP) is estimated to be -0.026 GPa⁻¹, which is almost the same as -0.025 GPa⁻¹ obtained by using the experimental results in Figure 154A. In Fe/Cr magnetic multilayers, Suenaga et al. (2007) reported that the MR of [Fe(2 nm)/Cr(3 nm)]₂₀ is enhanced strongly by an application of pressure. This result is different from the case of Fe/Tb multilayers as mentioned above. This may be resulted from a difference in spin structure and the interlayer coupling.

In summary, the suppression of MR of Fe/Tb multilayers is caused by both the effects of pressure on ΔR and R(0). Both effects are caused by the same origin, that is, by the change in magnetic states in the Tb layers. This is related to the suppression of the magnitude of MR by applying pressure.



FIGURE 154 Pressure dependences of (A) MR (8.5 T), (B) the electrical resistance at 0 T, and (C) the ΔR at 8.5 T of [Fe(12 nm)/Tb(15 nm)]₂₅ at 4.2 K (Ohashi et al., 2008).

6. SUMMARY AND CONCLUSION

In this chapter, we have reviewed the pressure studies of rare earth compounds having borderline electronic and magnetic states. These measurements under high pressure have been performed over several decades by using many kinds of experimental techniques. The effects of pressure on the physical properties of rare earth compounds are mainly dominated by the competition between the Kondo effect and RKKY interactions, which are the function of Kondo coupling $JN(E_F)$. On the basis of this consideration, the general phase diagram (the so-called

Doniach's phase diagram) has been constructed as a function of $JN(E_{\rm F})$ or pressure: the magnitude of *J* increases approximately with increasing pressure. The presented results are also discussed in connection with this phase diagram. We have reported the experimental results that have been obtained by using diffraction techniques, thermal expansion and heat capacity measurements, electrical resistance, and magnetic measurements under multiple extreme conditions, such as high pressures, high magnetic fields, and low temperatures.

In Section 2, the high-pressure studies of rare earth compounds using X-ray and ND techniques have been described. Structural transformations, volumes, and magnetic structures were examined under high pressure. The valence transition of Ce atoms was explored at high pressure, and the pressure-volume relationships are analyzed using equation of state. The large changes in the temperature dependence of electrical resistance are observed at high pressure, indicating a pressure-induced crossover in the electronic states. These results are combined with structural studies and then a pressure-induced valence transition is suggested to exist at room temperature and high pressure. No discontinuous change in volume has been observed around the valence transition. The anomalous elastic properties and a possible TPT were also pointed out for CeAl₂. The recent progress in the high-pressure ND techniques was briefly reported in this section, and the results obtained by using this new high-pressure apparatus are introduced to search for the new magnetic phases at high pressure. Close relationships between SC and magnetic order were also clarified at high pressure for UGe₂ and CeRhIn₅ compounds.

In Section 3, the thermal properties of rare earth compounds at high pressure have been reviewed. In Sections 3.1 and 3.2, the general survey and the recent progress in the measuring techniques are briefly discussed. Until now, there have been only a few publications on the thermal expansion measurements under pressure, which is mainly due to technical difficulties with such measurements. The heat capacity measurements under pressure have been reported in Section 3.3 for HF materials, CeIrSi₃, CeRhSi₃ and CeRhIn₅ compounds, and UGe₂, in which the interplay between magnetism and SC was investigated in details. The thermal expansion and specific heat of nonmagnetic narrow-gap semiconductor SmS and the phase transition and the magnetic properties under pressure were discussed. The thermal expansion measurements have been shown in Section 3.4 for a wide range of materials, including HF materials with or without magnetic order, and valence fluctuating materials. The overall behavior of these materials is largely different from one other. The relation between magnetic order and lattice properties is discussed on the basis of Doniach's phase diagram. The presented results indicate that the HF and valence fluctuating states are generally suppressed by the application of pressure. In other words, the electron correlation effects exhibit a tendency to disappear at high pressure. The effect of pressure on the magnetic ordering temperature seems to be complicated, but the results for antiferromagnetic order are explained qualitatively by Doniach's phase diagram. The anomaly in the thermal expansion coefficients observed in CeRh₂Si₂ and CeAu₂Si₂ may be related to the occurrence of SC. The MS of HF materials under pressure was also reviewed. The magnitude of MS decreases with pressure due to an increase in Kondo temperature.

Novel electronic phases at high pressure are discussed in Section 4. The pressure-induced crossovers in the electronic states in some HF materials are Summarized in Section 4.1 on the basis of electrical resistance measurements. Drastic changes in the temperature dependence of electrical resistivity are observed by applying pressure, and the temperature dependence was also analyzed in detail. Extremely large coefficients of T^2 dependence were observed at ambient pressure, and their magnitude is found to decrease significantly at high pressure. This fact implies that the effect of strong correlation is suppressed at high pressure. The HF states are collapsed and then show a crossover to a valence fluctuating state. The most recent topics in this research fields is to explore the pressure-induced SC and NFL behavior on the border of magnetic instability in highly correlated electron systems. Some typical examples with magnetic order are presented in Section 4.2. All materials mentioned in this section show pressure-induced SC- and NFLlike behavior near the QCP, where the ordering temperature becomes 0 at high pressure. The Grüneisen parameters were estimated from these data, and we conclude that pressure suppresses their magnitude indicating that the valence fluctuating states are stabilized at high pressure, and then the electronic state may become normal by further increases of pressure.

In Section 5, we mentioned some interesting materials including rare earth elements, which are expected to show novel pressure-induced electronic states. Generally speaking, the pressure suppresses the magnetic order as expected from the negative pressure coefficients of $T_{\rm C}$ or $T_{\rm N}$. Some rare earth compounds show magnetic order under uniaxial pressure or hydrostatic pressure. For CeNiSn, the relation between the magnetic order and lattice properties under uniaxial pressure is discussed. For YbInCu₄, the occurrence of magnetic order and SC at high pressure was discussed in connection with QCPs. In Section 5.2, amorphous materials including rare earth elements are briefly reviewed. It was found that the pressure dependence of the Kondo coupling $IN(E_{\rm F})$ is larger than in crystalline materials, and the Kondo temperature estimated from the data shows a stronger pressure dependence when compared with crystalline materials. But there may be some discrepancies between the available data. So at present, it may be safe to say that HF properties are sensitive to the arrangement of rare earth atoms. In Section 5.3, we showed high-pressure studies of magnetic multilayers including rare earth elements. In the nanoscale magnet, we expect novel electronic

properties under pressure. MR on the order of 8% was observed, but the enhancement of MR ratio by applying pressure was not found.

Finally, we want to emphasize that high pressure is an excellent tool to investigate the electronic structure particularly for materials that have unstable electronic states on the border of magnetic instability.

The volume of interesting data on rare earth compounds under high pressure which have been accumulated over the decades is large. Obviously, we could not mention all of them in this chapter. Interested readers are directed to a recent review describing both the progress and new trends in high-pressure research of highly correlated electron systems that are summarized in the following Proceedings of an International Conference, "Novel Pressure-induced Phenomena in Condensed Matter Systems," J. Phys. Soc. Jpn. 76, 2007 (edited by T. Kagayama, M. Ohashi, and Y. Uwatoko).

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CHAPTER 253

Thermodynamic Properties of Lanthanide Fluorides and Chlorides in the Gaseous and Condensed States

Alexandr D. Chervonnyi

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List of Acronyms and Symbols			
0	superscript indicating standard state of the substance		
$\angle (X - R - X)$	bond angle in polyatomic molecule ($X = F$, Cl)		
$\angle_{e}(X-R-X)$	equilibrium bond angle in polyatomic molecule $(X = F, Cl)$		
$\angle_{g}(X-R-X)$	bond angle for an effective thermal average configuration of polyatomic molecule ($X = F$, Cl)		
$A_1, E, A_u, B_{1u},$	symbols characterizing the electronic state		
B_{2u}, B_{3u}	symmetry in nonlinear polyatomic molecule		
aq	aqueous		
AE	appearance energy		
α	constant characterizing the crystalline solid at		
	thermal expansion		
α_1	rovibrational constant of diatomic molecule		
$\alpha_2, \beta_2, \omega_e y_e, \omega_e z_e$	molecular constants in diatomic molecule		
b_{i2}	mass spectrum coefficients		
β	isothermal compression coefficient of crystalline solid		

R.	rovibrational constant in diatomic molecule
p_1	rotational constant in diatomic molecule
D _e	applicational constant in diatonne molecule
$c_1,, c_5$	coefficients of the polynomial for heat capacity
°°	calculation at arbitrary temperature
C _{exs}	excess heat capacity
$C_{\rm d}$	the contribution to the heat capacity related to
	crystal thermal expansion
$C^{\circ}_{d,cor}(T)$	the correction contribution to the heat capacity
C_{e}°	the contribution to the heat capacity caused by
	electronic conductivity
C_{lat}	lattice heat capacity
$C_{\rm m}^{\circ}$	the contribution to the heat capacity related to
	cooperative magnetic ordering
$C_{n}^{\circ}(298)$	isobaric heat capacity at $T = 298.15$ K
$\hat{C}_{n}(lig)$	isobaric heat capacity in the liquid state
$C^{\circ}(T)$	isobaric heat capacity at arbitrary temperature
$C^{\circ}(T)$	isobaric heat capacity at arbitrary temperature
Cp,cal(1)	calculated from $\theta_{\rm D}$, $\theta_{\rm D}$, and α
C° (T)	isobaric heat capacity at arbitrary temperature
Cp,exp(1)	calculated from experimental data
C°_{a} .	the contribution of noncooperative magnetic
USch	ordering (the Schettky contribution)
C°	the lattice (vibrational) component of the isocharia
c_{v}	heat capacity
C	the neint example and the result
C_{2v}	the point symmetry group
C_{3v}	the point symmetry group
CN	coordination number
cr	crystal
$D(\Theta_{\rm D}/T)$	Debye function for heat capacity of crystalline solid
$D^{\circ}(0)$	bond energy in polyatomic molecule at $T = 0$ K
D_{2h}	the point symmetry group
D_{3h}	the point symmetry group
$D_{\rm e}$	centrifugal stretching constant in diatomic
	molecule
$\Delta G_{1/2}$	fundamental vibrational frequency in diatomic
	molecule
$\Delta_{ m at} H^{\circ}(0)$	enthalpy of atomization at $T = 0$ K
$\Delta_{ m at} H^{\circ}(298)$	enthalpy of atomization at $T = 298.15$ K
$\Delta_{\rm f} H^{\circ}(0)$	enthalpy of formation at $T = 0$ K
$\Delta_{\rm f} H^{\circ}(298)$	enthalpy of formation at $T = 298.15$ K
$\Delta_{\rm f} H^{\circ}({\rm cr}, 298)$	enthalpy of formation of crystalline solid at
	T = 298.15 K
$\Delta_{ m m} H^{\circ}$	enthalpy of melting

$\Delta_{\rm r} H^{\circ}(0)$	enthalpy of reaction at $T = 0$ K onthalpy of reaction at $T = 208.15$ K
$\Delta_{\rm r} H^{\circ}(298)$, II law)	enthalpy of reaction at $T = 298.15$ K, found from second law calculation
$\Delta_{ m r} H^{\circ}$ (298, III law)	enthalpy of reaction at $T = 298.15$ K, found from third-law calculation
$\Lambda H^{\circ}(0)$	enthalpy of sublimation at $T = 0$ K
$\Delta_{sub} H^{\circ}(298)$	enthalpy of sublimation at $T = 298.15$ K
$\Delta_{sub}H^{\circ}(298)$	enthalpy of sublimation at $T = 298.15$ K found
II law	from second-law calculation
$\Lambda_{\rm mb}H^{\circ}(298)$	enthalpy of sublimation at $T = 298.15$ K found
III law)	from third-law calculation
$\Delta_{\rm tr}H^{\circ}$	enthalpy of polymorphic transition
$\Delta_{uan} H^{\circ}(T)$	enthalpy of vaporization at arbitrary temperature
$\Delta_m S^\circ$	entropy change at melting
$\Delta_{\rm tr}S^{\circ}$	entropy change at polymorphic transition
$\Delta \ddot{V}$	change of molar volume of crystalline solid
DFT	density functional theory
$E(\Theta_{\rm Ei}/T)$	Einstein function for heat capacity of crystalline
	solid
ε_i	energy of <i>i</i> th electronic state
f_1, \ldots, f_7	coefficients of the polynomial for reduced Gibbs
	energy calculation at arbitrary temperature
g	gas
<i>8i</i>	degeneracy (statistical weight) of <i>i</i> th electronic
	state
$-[G^{\circ}(T) - H^{\circ}]$	reduced Gibbs energy related to $T = 0$ K
(0)]/T	
$-[G^{\circ}(T) - H^{\circ}]$	reduced Gibbs energy related to $T = 298.15$ K
(298)]/T	
γ	thermal expansion coefficient of crystalline solid
$H^{\circ}(T) - H^{\circ}(0)$	isobaric change in enthalpy above the temperature
	of 0 K
$H^{\circ}(T) = H^{\circ}(298)$	isobaric change in enthalpy above the temperature
7 7 7	of 298.15 K
$I_{R^+}, I_{RC1^+}, I_{RC1_2^+}, I_{RC1_2^$	the ion current intensities in the mass spectrum
$I_{\text{RC1}_{3}}, I_{\text{R}_{2}\text{C1}_{5}}$	in a institute of a state of DV and the state
$\frac{1E(KX)}{1E}$	ionization energy of KA molecule
$1E_1, 1E_2$	atoms of rare earth element
κ°	acoust of the reaction at a
Nр	equilibrium constant of the reaction at a
	constant pressure

LFT	ligand field theory
liq	liquid
v_1, v_2, v_3, v_4	fundamental vibrational frequencies in polyatomic molecule
ω_{e}	vibrational constant in diatomic molecule
$\omega_{e} x_{e}$	anharmonicity constant in diatomic molecule
p°	standard pressure (101,325 Pa)
$P_{\rm m}, P_{\rm d}$	partial pressure of monomeric and dimeric mole-
	cules, respectively
$\Phi_{ m el}^{\circ}$	electronic component of the reduced Gibbs energy
Q(T)	molecular partition function
r^{+}, r^{-}	the R^{2+} and Cl^{-} ion radii in the crystal lattice
R	universal gas constant (8.31447 J/(mol·K))
R(R-X)	interatomic distance in polyatomic molecule
. ,	(X = F, Cl)
R _e	interatomic distance in diatomic molecule
$R_{\rm e}({\rm R-X})$	equilibrium interatomic distance in polyatomic
	molecule ($X = F, Cl$)
$R_{\rm g}(\rm R-X)$	interatomic distance in polyatomic molecule
C	(X = F, Cl) for effective thermal average
	configuration
$S_{\rm exs}^{\circ}(298)$	excess entropy at $T = 298.15$ K
$S_{\rm lat}^{\circ}(298)$	lattice component of entropy at $T = 298.15$ K
$S_{\mathbf{m}}^{\circ}$	the contribution to the entropy related to
	cooperative magnetic ordering
<i>S</i> °(298)	entropy at $T = 298.15$ K
$S^{\circ}(T)$	entropy at arbitrary temperature
σ	symmetry number of the molecule
$\sigma_{\rm m\prime} \sigma_{\rm d}$	the ionization cross sections of monomeric and
	dimeric molecules, respectively
Т	temperature
T _e	electronic state energy in diatomic molecule
$T_{\rm m}$	melting temperature
$T_{\rm tr}$	temperature of polymorphic transition
$\theta_{\rm D}$	characteristic Debye temperature
$\theta_{\rm Ei}$	characteristic Einstein temperature
U°	crystal lattice energy
V	molar volume of crystalline solid
XAFS	X-ray absorption fine structure
$z_{\rm R}$, $z_{\rm Cl}$	ionic charge

1. INTRODUCTION

In recent years, the scope of application of lanthanides and their compounds has significantly expanded. They are widely used in the production of optical elements (plasma display panels, optic fibers in telecommunications), metal-halogen lamps, superconductors, highly selective catalysts, hydrogen batteries, magnetic alloys, fuel cells, etc. Scientific investigations of their magnetic, nuclear, optical, thermal, and chemical properties are realized for successful achievements in these fields.

With specific reference to lanthanide fluorides and chlorides, the main interest in their study has long been associated with the development of extraction processes of 4f elements from the mineral concentrates. Implementation of these processes usually occurs in melts at elevated temperatures (Kilbourn, 1997). The choice of lanthanide halides for this purpose is due to their relatively low melting points and high vapor pressures. Effective ways of obtaining 4f metals in high purity continue to evolve, despite the widespread consumption of lanthanide products containing a mixture of R-cations. Of special interest is the use of complex gaseous species RAl_nCl_{3n+3} formed with aluminum halides (Jiang et al., 1997). A process involving selective reduction and vacuum distillation of lanthanide halides (Il'in et al., 1976) has been consequently developed, which yielded a separation factor of 570 (Uda et al., 2000) for the Nd–Sm system. This is dramatically different from the 2.2 to 9.6 value, characteristic of ordinary solvent extraction processes.

Formation of such complex compounds, but already with alkali-metal halides, has found application in the manufacture of modern metal halide lamps (Born et al., 2004; Hilpert and Niemann, 1997), which have an emission spectrum close to that of the natural sunlight. Relevant iodides and bromides (particularly cerium and dysprosium bromides and iodides) were found to be the most suitable components of binary compounds for the production of lamp vessels from silica glass (Markus et al., 2005). Further technological developments led to the replacement of vessel material by polycrystalline alumina and to the use of rare-earth chlorides for improving lamp characteristics (Rutkowska et al., 2004).

Interest for lanthanide halogenides (here and hereinafter, fluorides and chlorides are referred to as halogenides) is growing due to problems in the field of nuclear technology. Indeed, some lanthanides (La, Ce, Pr, Nd, Sm, Eu, and Gd) are directly part of radioactive wastes (RAWs) (Baluev et al., 2000). In addition, the presence of actinides is often mimicked by 4f-metal compounds in the model mix of waste when studying the behavior of matrix materials *in vitro* (Kotel'nikov, 1995; Yudintsev et al., 1998). For instance, the volume of liquid and solid RAWs of various activity levels accumulated in Russia reaches about 500 and 177 million tons, respectively (Shatalov, 2002). Thus, the development of a large-scale process for the production of the material providing RAW immobilization (in accordance with the requirements of the International Atomic Energy Agency, IAEA) with high energy and economic efficiency is very urgent.

The modern concept of RAW management suggests the immobilization of the wastes into solid matrices which possess chemical, mechanical, and radiation resistance. Thus, the goals of immobilization (as a rule, solidification) are to decrease the waste volume, to remove liquids, and to reduce the mobility of radionuclides after their disposal. According to the IAEA requirements (Technical Reports, 2003), the radionuclide-containing matrix should provide irreversible immobilization under the conditions of prolonged storage and disposal (Technical Reports, 2001).

The most appropriate form of RAW is an oxide. However, the development of other technological schemes calls for recycling waste in the form of fluorides, and, even, chlorides, and their input into the matriximmobilizer, for example, in the process of hot isostatic pressing (McFarlane et al., 1997).

The above examples describe only in part the application scope of the compounds considered because in academic and technological centers, researchers continue to uncover new opportunities to use these compounds thanks to a deeper understanding of their properties. These examples show that there is an urgent need for a description of the thermodynamic properties (reduced Gibbs energy, heat capacity, entropy, enthalpy, enthalpy of formation at standard conditions) of the lanthanide halides for predicting their behavior in a wide temperature range when they enter into various processes.

The last explanation leads to the conclusion that full thermodynamic modeling of high-temperature processes requires knowledge not only of the thermodynamic functions of the condensed state in the appropriate temperature range but also of their gaseous state. As follows from the experimental data (Gmelin Handbook, 1982), all rare-earth elements form trifluorides and trichlorides in the condensed state, and only some of them (Sm, Eu, and Yb) are stable as dihalides in a wide range of temperatures. The existence of these compounds in the gaseous state is possible not only with the preservation of the valence state of lanthanide ions but also in the form of mono- and dihalides (in a reducing medium). Hence, the completeness of calculations (and, consequently, their reliability) is ascertained by the presence of data on thermodynamic properties of the molecules $RF_3(g)$, $RF_2(g)$, and RF(g) or $RCl_3(g)$, $RCl_2(g)$, RCl(g), and $R_2Cl_6(g)$. The inclusion of the $R_2Cl_6(g)$ molecules means that unlike trifluorides the trichlorides form gaseous dimers in appreciable quantity.

Experimental thermodynamic data for lanthanide compounds have continuously been summarized during the past decades (see, e.g., Myers

and Graves, 1977a; Pankratz, 1984; Wagman et al., 1982). And this is inevitable, as the improvement of preparative methods makes it possible to obtain purer substances which, in turn, leads to reexamination of their thermochemical properties. Also, the development of experimental techniques and new methods for measuring various molecular properties initiates measurement of new data. Collection and systematization of thermodynamic functions for fluorides and chlorides have been reviewed by Barin (1995). The data available in handbooks (Barin, 1995) at that time were, however, not the complete set of thermochemical characteristics. Data pertaining to condensed state have only been described for a number of compounds, and there were no thermodynamic functions for monohalides and dimers. Moreover, the partial data partly presented were obtained from correlation estimates of the properties of one compound based on the experimental data of the other without considering 4f-shell excited electronic states.

For example, proper accounting of electronic excitation influences the thermal characteristic result obtained from the measurement of low-temperature heat capacity in a temperature range from close to 0 K up to ~350 K. Although these studies were largely directed at the determination of the heat capacity C_p° (298) and entropy S° (298) values at standard temperature (298.15 K), they were also concerned with proving the existence of contributions to the heat capacity (as well as, entropy) of lanthanide compounds induced by excitation of electronic states. Significant and distinctive changes in C_p° (298) and S° (298) values were found for most lanthanide compounds. That is, the existence of the so-called Schottky anomaly in thermal parameters was established.

Similarly, such a problem must be solved by describing the thermodynamic properties of gaseous molecules. For example, Myers and Graves (1977a) calculated thermodynamic functions including electronic excitation contributions. They used the electronic excitation of triply charged lanthanide ions in crystals. But such an approach does not describe accurately the temperature dependence of thermodynamic functions. It would be better to take into account the effect of Stark splitting of lowlying electronic states on thermodynamic functions.

A limited and often contradictory set of available experimental data was the main obstacle to the solution of these problems. A general belief that their solution is possible only by systematic analysis of the molecular and macroscopic properties of the compounds studied emerged in the course of dealing with these problems and critically evaluating thermal and thermochemical data, in spite of the fairly large material accumulated to identify the patterns of changes in thermal characteristics of the series of similar compounds (see relevant sections in Gurvich et al., 1978–1984; Spencer, 1998). Therefore, our first goal is to use a system of evaluations and correlations capable to estimate the reliability of the available experimental data. A second goal is to find appropriate computational procedures or criteria for obtaining missing data.

Up to now, no attempt has been made to merge the low-temperature heat capacity data with the high-temperature enthalpy increment data, to yield a consistently assessed correlation covering the temperature range from T = 0 up to T_m (or T_{tr}) where T_m is the melting point and T_{tr} is the temperature of the polymorphic transition. It is usually inferred that it is impossible to carry out computations using polynomial approximations for $C_p^{\circ}(T)$ to derive polynomial expressions for the entire temperature range.

In the case of lanthanide trihalides, we endorse the computational method of heat capacity calculations in a wide interval of temperatures (from about T = 0 to $T_{\rm m}$), based on the analysis of the experimental values of the low-temperature heat capacities, $C_{\rm p,exp}^{\circ}(T)$. High-temperature enthalpy increments are used for correcting $C_{\rm p,cal}(T)$ values in the range of temperature $T > \sim 0.5T_{\rm m}$. Such an approach removes the restriction of quasi-harmonic approximation of a heat capacity in this temperature range.

For RX₃ (R = La–Lu) molecules, regularities in the behavior of various parameters in the equation describing the lattice heat capacity in quasiharmonic approximation are revealed from the available values of lowtemperature heat capacity. These parameters have a linear dependence on molar volume for compounds with identical crystalline structure. As a result, it becomes possible to define these parameters and to subsequently calculate heat capacities in a wide interval of temperatures for unexplored compounds.

Application of this method in the calculation of thermodynamic functions leads to small differences in enthalpy and reduced Gibbs energy estimated from $C_{p,cal}^{\circ}(T)$ and $C_{p,exp}^{\circ}(T)$ values. Using this method, a significant amount of thermodynamic properties for halides was obtained for the first time for a number of lanthanides.

Also, we were able to describe methods for estimating and processing available experimental data for selected parameters (e.g., calculation of contributions to the heat capacity caused by electronic excitation in the full temperature range, or consideration of structural features of the melt and their influence on the heat capacity in the liquid state).

All this together with the newly calculated thermodynamic functions of gaseous compounds required the development of procedures for evaluating the reliability of the complete set of thermodynamic parameters. The selected approach involves calculation of the atomization and/or sublimation enthalpy under standard conditions from the vapor pressure measurements. The same values are calculated from the data found by other independent methods (electron-impact ionization, measurement of gas-phase equilibria). The convergence of values found in various ways demonstrates the reliability of the thermodynamic functions and their possible use in practical calculations.

The above-mentioned procedure is also useful with respect to the description of new relationships for series of similar compounds. Some special features of changes in the sublimation enthalpy over series of such compounds are well seen in the dependence of $\Delta_{sub}H^{\circ}(298)$ on the position of the 4f metal in the lanthanide series. A decrease in the coordination number (CN) of a 4f metal in the crystal lattice of the corresponding compound leads to a lower $\Delta_{sub}H^{\circ}_{298}$ value. This is observed in going from β -YF₃- to LaF₃-type structures of the trifluorides. A similar phenomenon is characteristic for the lanthanide trichlorides and dichlorides. Moreover, the absolute value of the sublimation enthalpy reflects the stability of the compound and its resistance to thermal actions. As expected, such correlations are typical for other series of similar 4f compounds.

The results obtained are presented in the form of the equation

$$-\frac{[G^{\circ}(T) - H^{\circ}(0)]}{T} = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3$$

where $x = T \times 10^{-4}$, approximating the reduced Gibbs energy with high accuracy. These data are given within the range 298.15–3000 and 298.15–2000 K for gaseous and condensed states, respectively. If necessary, the coefficients of the equation can be used to determine other thermodynamic functions (entropy, heat capacity, enthalpy) of the compounds under consideration

$$\begin{split} S^{\circ}(T) &= f_1 + f_2 + f_2 \ln x - f_3 x^{-2} + 2f_5 x + 3f_6 x^2 + 4f_7 x^3, \\ C^{\circ}_{\rm p}(T) &= f_2 + 2f_3 x^{-2} + 2f_5 x + 6f_6 x^2 + 12f_7 x^3, \\ H^{\circ}(T) - H^{\circ}(0) &= 10 (f_2 x - 2f_3 x^{-1} - f_4 + f_5 x^2 + 2f_6 x^3 + 3f_7 x^4). \end{split}$$

For all compounds under investigation, the enthalpy of sublimation (for condensed state), $\Delta_{sub}H^{\circ}(0)$, the enthalpy of atomization (for gaseous state), $\Delta_{at}H^{\circ}(0)$, as well as the enthalpy of formation at T = 0 K, $\Delta_{f}H^{\circ}(0)$, and the enthalpy of formation at T = 298.15 K, $\Delta_{f}H^{\circ}(298)$, are obtained. Such a representation is universally accepted, as it can be readily used not only in electronic thermochemical reference databases (such as IVTANTERMO, 2004) but also in relevant programs for the calculation of thermodynamic equilibriums.

It must be emphasized that the rule formulated by Gurvich (1983) was followed in all cases where this was possible. It consists in the fact that the systematization and the processing of results in the preparation of the reference data are carried out only with primary data, that is, with data directly measured in a particular experiment and not obtained by further processing of the results using a variety of auxiliary constants. In original papers, the representation of the reduced Gibbs energy as the Gibbs energy function (format of "NIST-JANAF Thermochemical Tables," see Chase, 1998; Chase et al., 1985), $-[G^{\circ}(T) - H^{\circ}(298)]/T$, is often used. The above equation for the reduced Gibbs energy can be easily translated into the following format:

$$-[G^{\circ}(T) - H^{\circ}(298)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4^* x^{-1} + f_5 x + f_6 x^2 + f_7 x^3,$$

in which all the f_i coefficients retain the previous value except f_4 . The new f_4 value is equal to $f_4^* = f_4 + [H^{\circ}(298) - H^{\circ}(0)]/10$, with the $H^{\circ}(298) - H^{\circ}(0)$ value in kJ/mol.

In general, the present review describes some fundamental properties of the studied compounds, which, nevertheless, have an independent role for the solution of a number of scientific and applied problems. Accumulated knowledge acquires a fundamental significance due to the fact that the developed system of calculations and evaluations can be used to describe the thermodynamic properties of unexplored or poorly studied related compounds. It is also promoted by the correlations found between the electronic structure of the lanthanides and the properties established on the molecular and macroscopic levels for the considered compounds.

The results collected here have been preliminarily published in "The Russian Journal of Inorganic Chemistry" and in "The Russian Journal of Physical Chemistry" (Publisher—Pleiades Publishing, Ltd.). The aim of the review is to describe the techniques and methods for calculating the thermodynamic functions of individual compounds and estimating missing data based on examples which provide satisfactory accuracy of the final results.

2. THERMODYNAMIC FUNCTIONS FOR LANTHANIDE TRIHALIDE MOLECULES

The thermodynamic functions (and other properties needed for their calculations) of gaseous lanthanide trichlorides have been extensively studied for several decades. In our view, the primary data on molecular constants are adequate for the required revision and refinement of the reduced Gibbs energy for the compounds under consideration. Moreover, this class of compounds perfectly demonstrates how the contribution from electronic excitation to reduced Gibbs energy can be considered. Therefore, we start by describing the properties of RCl₃ (R = La–Lu) molecules.

2.1 Thermodynamic functions for lanthanide trichloride molecules

A complete summary of the thermodynamic functions of RCl₃ was given for the first time by Chervonnyi (1975). These data are for a limited temperature interval and became commonly accessible (Chervonnyi,

1977b) virtually simultaneously with the calculations by Myers and Graves (1977a). In both works, the functions were calculated for the ideal gas state at temperatures up to 2000 K and standard pressure in the rigid rotator-harmonic oscillator approximation with the use of standard equations (Chase et al., 1985; Gurvich et al., 1978-1984). The necessary molecular constants (vibrational frequencies, \angle (Cl-R-Cl) angle values, and interatomic distances) were estimated from a limited number of experimental data. The independent approaches to estimating molecular constants, however, gave closely similar results. The difference in reduced Gibbs energies $- [G^{\circ}(T) - H^{\circ}(0)]/T$ ranged between 0.8 and 11.8 J/(mol·K) for the lanthanide trichloride series (for T = 1000 K). This difference was caused by two reasons. First, Chervonnyi (1975, 1977b) performed calculations for pyramidal structures (C_{3v} symmetry), whereas Myers and Graves (1977a) used a planar molecular geometry (D_{3h} symmetry). Accordingly, the $- [G^{\circ}(T) - H^{\circ}(0)]/T$ values obtained for pyramidal molecules were higher by Rln(2). Next, Myers and Graves (1977a) were able to more correctly include the electronic excitation energy by taking into account the energy levels up to 5000 cm⁻¹, which increased the reduced Gibbs energy values.

Since then, some new data on molecular parameters were obtained, and the range of compounds studied was broadened. But molecular constant variations (probably except the symmetry number) do not influence thermodynamic function values very substantially. A much stronger effect is that of the contribution of the electronic component. It should be taken into account that lanthanide compounds have a large number of excited electronic states. Although molecular constants for these states are unknown, their contribution to the thermodynamic functions can be considered by introducing a calculated correction (Gurvich et al., 1978– 1984) to the electronic ground-state component. For ionic compounds such as lanthanide halides, the correction can be calculated using the electronic excitation energies of free \mathbb{R}^{3+} ions (Martin et al., 1978).

But it was necessary to consider the Stark splitting of the ground electronic states of the central atom in ligand field. Inclusion of this splitting noticeably influences the electronic component value (Φ_{el}) in the reduced Gibbs energy, especially at low temperatures. Therefore, new calculation of thermodynamic functions of RCl₃(g) has been performed (Chervonnyi and Chervonnaya, 2004g), and the main results reported by these authors are considered in this section.

2.1.1 Molecular constants

As has been mentioned, selecting the geometry for the compounds under consideration is of importance for calculating their thermodynamic constants. The symmetry number used in calculations takes on the values 3 or 6 depending on whether the molecules are assigned a pyramidal or planar geometry. The available data on the molecular constants allow us to assert with definiteness that lanthanide fluorides are pyramidal. Conversely, lanthanide iodides are predicted to have planar or at least quasi-planar geometries (Hargittai, 2000). By analogy with the definition of "quasilinear" molecules formulated by Hargittai (2000), "quasi-planar" molecules are understood to have a very low energy barrier to the transition between pyramidal configurations, low to the extent that the transition becomes possible under heat action. Such changes in the shape of molecules are largely caused by an increase in the size of the ligand and a decrease in its polarizing action.

The general tendencies of changes in molecular constants along a series of lanthanide compounds are also well known. Because of the lanthanide contraction in going from lanthanum to lutetium, various constants decrease or increase monotonically. The question of the shape of lanthanide trichlorides therefore becomes very important. Indeed, these molecules can be pyramidal, or planar, or pyramidal for lanthanum but gradually flattening to planar as we go to lutetium.

Seemingly, the available experimental data (Feltrin and Nunziante-Cesaro, 1996; Kovács and Konings, 1997; Kovács et al., 1995, 1997; Loktyushina et al., 1984, 1987; Perov et al., 1975; Selivanov et al., 1973; Wells et al., 1977) on vibrational frequencies observed in the IR spectra of lanthanide trichlorides should give an unambiguous answer to the question of the shape of these molecules. Although there are abundant experimental and estimated data on vibrational frequencies, we only discuss here results and estimates based on experimental works. If the spectra contain the symmetrical stretching vibration band v_1 , the molecules should be pyramidal because this mode is forbidden D_{3h} symmetry. Indeed, several authors assigned the observed IR bands to symmetrical stretching vibrations. The question, however, arises of the correctness of this assignment. The matter is that we have $v_1 > v_3$ for trifluorides (Boghosian and Papatheodorou, 1996; Hargittai, 2000; Kovács, 2000) and $v_3 > v_1$ for bromides and iodides (Kovács, 1999, 2000). Which relationship between these frequencies should be expected for RCl₃? For instance, theoretical calculations (Hargittai, 2000) for planar ScCl₃ and YCl₃ give lower symmetrical stretching vibration frequencies compared with their antisymmetric counterparts.

Interpretation of IR spectra therefore becomes fairly intricate. According to Hargittai (2000), electron diffraction data, most of which favor the pyramidal structure of RCl₃, also do not give an unambiguous answer to the question of the structure of trichlorides. Indeed, even when the structural parameters are determined from primary electron diffraction data with harmonic analysis methods, this analysis is based on vibrational frequencies, either obtained from experimental spectra or estimated, but the complex vapor composition of these compounds is not taken into account. However, the use of empirical dependences can lead to serious errors. In this respect, an instructive example is provided by the work of Kovács et al. (1995), where CeCl₃, NdCl₃, SmCl₃, GdCl₃, and DyCl₃ were studied. Despite performing various *ab initio* calculations, the authors had to renounce to use their results for reinterpreting the IR spectra of these compounds (Kovács and Konings, 1997).

More definite conclusions about the structure of the compounds under consideration can be drawn from theoretical calculations of their geometry and vibrational frequencies. In the past decade, more than a dozen of works concerned with lanthanide trichlorides have been published (Adamo and Maldivi, 1997, 1998; Di Bella et al., 1993; Jansik et al., 2002; Joubert et al., 1998a,b; Kovács, 2000; Solomonik and Marochko, 2000a; Tsuchia et al., 1999; Vetere et al., 2000).

2.1.2 Theoretical structure calculations

Let us consider the principal results of these calculations in the case of lanthanum trichloride, for which the most complete *ab initio* and density functional theory (DFT) calculations (both with various basis set modifications) are available. The obtained molecular parameters strongly depend on the valence basis sets and effective relativistic core potentials. Nevertheless, *ab initio* calculations tend to predict a planar structure, whereas DFT calculations favor pyramidal configurations. The v_2 frequencies obtained in all calculations are too low compared with those found experimentally. This implies a low barrier to inversion and large thermal geometry fluctuations. In view of such uncertainty in the results of quantum-chemical calculations, Hargittai (2000) was very careful in her estimates. She tends to favor the planar geometry of lanthanide chlorides, although does not rule out the possibility that they are pyramidal.

However, in the paper authored by Kovács (1999) and published almost simultaneously with the work of Hargittai (2000), the author proves pyramidality of LaCl₃ and DyCl₃ on the basis of DFT calculations. We note that similar conclusions were drawn earlier by Joubert et al. (1998b), Adamo and Maldivi (1997, 1998). In addition, simultaneously, the structual parameters for dimers were simultaneously established. The intensities of the IR bands of dimers and monomers give a sound explanation as to why the v_1 band could not be identified in the spectra of lanthanide trichlorides. It was found that the difference of the vibrational frequencies between dimers and monomers is so small and the intensity ratio between the corresponding bands is such that a dimer content of ~1% is sufficient to mask the symmetrical stretching vibration in vapors of these compounds (whose intensity is low) by the bands of these dimers. Note that the vibrational frequencies obtained by Kovács (1999) are closest to the experimental data (Selivanov et al., 1973) on LaCl₃. Simultaneously, somewhat less satisfying agreement ($v_1 > v_3$) was obtained by Vetere et al. (2000).

As far as the equilibrium configuration in the series of lanthanide trichlorides is concerned, the compounds calculated by the DFT method are lanthanum and dysprosium (Kovács, 1999) and lanthanum, gadolinium, and lutetium (Adamo and Maldivi, 1997, 1998; Joubert et al., 1998b; Vetere et al., 2000) halides. Considering the tendency of changes in the \angle (Cl-R-Cl) angle for chlorides, the results of these calculations seem to agree with each other. Equilibrium pyramidal configurations are characteristic of all lanthanide chlorides except LuCl₃. The configuration of LuCl₃ is either pyramidal (Kovács, 2000) or planar (Adamo and Maldivi, 1997, 1998; Vetere et al., 2000). Moreover, not only all trifluorides but also LaBr₃ and LaI₃ have pyramidal geometries.

The calculated barrier to the transition from a pyramidal to a planar configuration and in the opposite direction is very low and varies depending on the calculation procedure. In particular, according to Vetere et al. (2000), the DFT/PBE0 procedure yields barrier values of 0.71, 0.33, 0.08, and 0.04 kJ/mol for lanthanum trihalides from trifluoride to triiodide, respectively. Of greater importance is another conclusion made by Kovács et al. (1997) and substantiated by theoretical calculations in more recent works. The low out-of-plane bending vibrational frequencies v_2 obtained in calculations are caused by the use of the harmonic approximation. In reality, these vibrations are anharmonic, and the v_2 values are much higher. Unfortunately, taking into account anharmonic effects is currently impracticable for lanthanide trichlorides.

The results of quantum-chemical calculations of the structure and vibrational spectra of LaCl₃ reported in Solomonik and Marochko (2000a) require a separate discussion with invoking similar calculations of LaF₃ published earlier by the same authors (Solomonik and Marochko, 2000b). According to Solomonik and Marochko (2000a,b), lanthanum trichloride is planar and lanthanum trifluoride pyramidal (\angle (F—R—F) = 117.5°). In addition, it follows from the calculations that LaCl₃ has a very low out-of-plane bending vibration frequency $v_2 = 6$ and 12 cm⁻¹, respectively). The barrier to inversion was found to be very low for LaF_{3} , $h = E(D_{3h}) - E(C_{3v}) = 39$ cm^{-1} (~ 0.45 kJ/mol). Agreement between the calculation results and experimental data being quite satisfactory for the other frequencies, the observed discrepancy for the v_2 vibrational mode was explained by possible correspondence of the IR band to one of the overtone vibrational transitions in the molecule under consideration. In particular, the 81 and 84 cm⁻¹ bands assigned to v_2 in the IR spectrum of LaF₃ (Hastie et al., 1975; Wesley and DeKock, 1971) can, for instance, correspond to the $0 \rightarrow 4$ transition. The potential energy function for out-of-plane deformations of the LaF₃ molecule has two minima corresponding to pyramidal configurations which are separated by the barrier of inversion corresponding to the planar



FIGURE 1 Potential energy function of the out-of-plane bending vibration and vibrational energy levels (*horizontal lines*) calculated by Gorokhov and Osina (2002) and in the harmonic approximation (*on the right*) for lanthanum trifluoride; ρ is the angle between the La–F bond and the normal to the threefold symmetry axis.

configuration (see Figure 1). This and a comparison of the vibrational energy levels calculated by the variational method and in the harmonic approximation led the authors to conclude that the potential of out-of-plane deformations could not be described by the harmonic oscillator model. This potential was also found to be anharmonic for the LaCl₃ molecule with a planar structure. Similar out-of-plane potential functions were reported in Kovács et al. (1997) for LaCl₃, LaBr₃, and LaI₃ and in Joubert et al. (1998b) for LuF₃ and LuCl₃.

We do not mean to minimize the importance of these results. Note, however, that the previously mentioned barriers of inversion calculated by Vetere et al. (2000) are approximately twice as high as in Solomonik and Marochko (2000a). In addition, it follows from the positions of the vibrational levels and the form of the potential energy function for LaF₃ (see Solomonik and Marochko, 2000b) that the two vibrational levels are situated below the barrier to inversion. However, according to Spiridonov et al. (2001), there are four such levels in LaCl₃, although the barrier is certainly lower than that for LaF₃. This is substantiated by the values obtained for the inversion barrier in LaCl₃ by Myers and Graves (1977a) and Kovács et al. (1995). The first authors estimated the inversion barrier $LaCl_3$ to be approximately 3 kJ/mol. These discrepancies are not related to some errors but are caused by the high sensitivity of the final results of quantum-chemical calculations to small changes in the basis set (Jansik et al., 2002; Kovács and Konings, 1997).

The general conclusion that follows from the review of the theoretical works cited above is that lanthanide halides are structurally nonrigid compounds with respect to out-of-plane bending motions, the vibrational frequency of which is anharmonic. However, a description of this anharmonicity for lanthanide chlorides was lacking. It was established later and the results of reduced Gibbs energy calculations under anharmonic approximation will be described subsequently. In this situation, the description of the v_2 vibration in the harmonic approximation is currently the only possibility for calculating thermodynamic functions. A somewhat contradictory character of the final results of various theoretical approaches leads us to preferably use experimental data for estimating molecular parameters of the compounds under consideration.

2.1.3 Estimation of vibrational frequencies from IR spectra

Because of the masking effect of dimeric molecules mentioned above, the arising of a large number of vibrational and rotational excited states of the initial molecules at high temperatures, and the similarity of the stretching $(v_1 \text{ and } v_3)$ and bending $(v_2 \text{ and } v_4)$ vibration frequencies, the IR spectra of lanthanide trichlorides have low resolution. Several authors (Feltrin and Nunziante-Cesaro, 1996; Kovács and Konings, 1997; Kovács et al., 1995, 1997; Loktyushina et al., 1984, 1987; Perov et al., 1975; Selivanov et al., 1973; Wells et al., 1977) were nevertheless able to determine the v_3 frequency. Leaving aside the data from Kovács et al. (1995), which, as has been mentioned above, were revised by the authors themselves, and the results reported by Wells et al. (1977), which are questionable because of the ratio between the v_1 and v_3 frequencies and the too high v_3 and v_4 values reported in that work, the experimental data and frequency estimates agree well with each other considering the tendency of v_3 variations in a series of similar lanthanide compounds. It should only be borne in mind that the frequencies obtained by Perov et al. (1975) in a xenon matrix have a larger red shift (by $\sim 15 \text{ cm}^{-1}$) than those in an argon matrix. Similar differences were observed by Loktyushina and Mal'tsev (1984) in the case of some lanthanide tribromides and triiodides.

If the data of Perov et al. (1975) are also excluded, the remaining results show a monotonic dependence on the atomic numbers of the lanthanides, which parallels the effect of lanthanide contraction. Such dependences can be described by the second-order polynomial:

$$P_i(n) = A_i + B_i n + C_i n^2, \tag{1}$$

where $P_i(n)$ is the molecular constant and *n* is the number of the central atom in the series of lanthanides (n = 1-15 for the series La–Lu).

This approach was precisely used to analytically describe molecular constants in this work. The coefficients of each polynomial were found by the least-squares fits of the corresponding experimental data.

The coefficients of the polynomial describing the atomic number dependence of v_3 were calculated from the data of Selivanov et al. (1973) for LaCl₃ and NdCl₃, the data of Feltrin and Nunziante-Cesaro (1996) for NdCl₃, DyCl₃, and TmCl₃, and from all values reported by Loktyushina et al. (1984, 1987), Kovács and Konings (1997), and Kovács et al. (1997). The resulting antisymmetric stretching vibration frequencies for lanthanum and dysprosium chlorides were lower (to within several cm⁻¹) than those calculated by Kovács (2000).

The spread of v_1 values was wider. We can distinguish between two series of v_1 frequencies. Comparatively low estimates for this frequency were obtained by Perov et al. (1975), where the vibrational spectra of lanthanum, gadolinium, and lutetium trichlorides were studied in xenon matrices. The first experimental measurements of v_1 were made much later by Loktyushina et al. (1987). Under matrix isolation conditions (large dilution), a doublet with v_1 slightly larger than v_3 was observed in the IR spectrum of HoCl₃. This assignment was substantiated by valence force field calculations for the pyramidal structure. Bond angle variations from 107° to 117° did not change the relative positions of the v_1 and v_3 frequencies but only influenced the distance between them, which changed from 18 to 3 cm⁻¹.

The analysis of theoretical calculations performed for lanthanum trichloride shows that, in spite of the use of different calculation procedures, all authors except Adamo and Maldivi (1997, 1998) and Vetere et al. (2000) report v_1 frequencies lying below v_3 . This prompted us to carefully analyze the work by Loktyushina et al. (1984) and the FTIR spectra of neodymium, dysprosium, and thulium trichlorides reported by Feltrin and Nunziante-Cesaro (1996).

In Feltrin and Nunziante-Cesaro (1996), a detailed analysis of the spectrum of NdCl₃ augmented by valence force field calculations was performed. The symmetrical stretching vibration frequency was sought based on the planar structure. The calculated v_1 frequencies of isotopic varieties of neodymium trichloride were in the range 272.7–280.3 cm⁻¹; according to the authors, some of these vibrations should be active in IR absorption. However, none was observed experimentally. On the other hand, a group of bands was recorded in the region characteristic of v_3 vibrations. The four central bands in this group (spaced by less than 3 cm⁻¹) were assigned to antisymmetric stretching vibrations of NdCl₃ isotopic varieties. As a result, the upper band (two bands for DyCl₃ and TmCl₃) and two lower bands remained unassigned. It was, however,
mentioned that the temperature dependence of the group of v_3 bands was different from that of the unassigned ones.

It is here pertinent to recall the results of theoretical calculations of vibrational frequencies and their intensities for monomers and dimers of lanthanum and dysprosium trichlorides (Kovács, 2000). In the series of vibrational frequencies, the v_3 vibration of the monomers lies between the two most intense frequencies of the dimers, while the v_1 mode, with low intensity, is situated below these three frequencies. A direct comparison of these frequencies for DyCl₃ with the experimental ones (Feltrin and Nunziante-Cesaro, 1996) reveals a close agreement. This suggests that the 315.4, 327.8, and 333.3 cm⁻¹ frequencies observed for NdCl₃, DyCl₃, and TmCl₃, respectively, correspond to symmetrical stretching vibrations. The spectrum obtained by Feltrin and Nunziante-Cesaro (1996) had higher resolution that those reported by Loktyushina et al. (1984) for the products formed in the interaction of lanthanide atoms with molecular chlorine in an argon matrix. The shape of the band assigned by Loktyushina et al. (1984) to antisymmetric stretching vibrations in lanthanide trichlorides (especially its low-frequency shoulder for GdCl₃) was, however, similar to that of the band of NdCl₃ reported by Feltrin and Nunziante-Cesaro (1996).

The data obtained by Feltrin and Nunziante-Cesaro (1996) for NdCl₃, DyCl₃, and TmCl₃ were described by a polynomial, which was used to calculate the v_1 values for the whole series of molecules under consideration. Their values were found to be 8.8–11.2 cm⁻¹ lower than v_3 for LaCl₃ through LuCl₃.

Much less experimental data are available for the bending vibrational frequencies v_2 and v_4 of lanthanide trichlorides.

The v_2 band was recorded in a xenon matrix by Perov et al. (1975) and in the gas phase by Wells et al. (1977) and Kovács et al. (1995, 1997). The data reported by Wells et al. (1977) are however unreliable. On the other hand, the results obtained by the other authors are satisfactorily consistent, considering matrix effects. In our estimates, we did not introduce corrections for the influence of matrices on the v_2 frequency but restricted ourselves to the frequencies reported by Kovács et al. (1995, 1997). Note that the ratio between vibrational frequencies (e.g., v_1/v_3 for the v_1 and v_3 values accepted in this work) remains constant to high accuracy in series of like lanthanide compounds. Bearing this in mind, we determined the mean frequency ratio v_1/v_3 . For this purpose, the v_3 values were calculated from the polynomial found above, and the v_2 frequencies were taken from Kovács et al. (1995, 1997). This ratio was used to calculate v_2 for the whole RCl₃ series. The results were exaggerated compared with theoretical calculations and were close to the experimental v_4 values. This closeness was in agreement with the predictions made by Kovács et al. (1997).

The v_4 values can be divided into two groups after excluding the value reported by Wells et al. (1977). The first set of data was obtained by Perov et al. (1975), who recorded the spectra of LaCl₃, GdCl₃, and LuCl₃ in xenon matrices at 20–30 K. The same work contains an estimate for the v_4 frequency for ErCl₃. These data fit well into the monotonically increasing curve describing the dependence of the frequency on the lanthanide atomic number. The second group includes the data reported by Kovács et al. (1995), which were obtained by primarily processing the IR spectra. However later, the authors (Kovács and Konings, 1997; Kovács et al., 1997) gave arguments for unreliability of their previous assignment of the v_4 frequency (Kovács et al., 1995), upon analysis of the 40–70 cm⁻¹ band.

The theoretically calculated v_4 frequencies (Kovács, 2000) were close to the results reported by Perov et al. (1975). We therefore accepted that the v_4 frequency could be described by the polynomial mentioned above, the coefficients of which were calculated using the data from Perov et al. (1975).

2.1.4 Interatomic distances and bond angles

Systematic gas-phase electron diffraction studies have been performed by several authors (Akishin et al., 1959; Danilova, 1978; Giricheva, 1975; Giricheva et al., 2000a,b,c,d; Krasnov et al., 1978, Spiridinov et al., 1990, 2001; Zasorin, 1988) to obtain data on atomic spacings R(R-Cl) and bond angles \angle (Cl-R-Cl) for a fairly wide range of lanthanide trichlorides, including LaCl₃, PrCl₃, NdCl₃, GdCl₃, TbCl₃, HoCl₃, ErCl₃, TmCl₃, and LuCl₃. In the first electron diffraction study of the structure of lanthanum and neodymium trichlorides, the authors concluded that these molecules were planar (Akishin et al., 1959), but this is the only study with such a conclusion. Indeed, according to Zasorin (1988), this result cannot be considered as being reliable because planarity was introduced into the initial structure analysis conditions. The data of the other electron diffraction experiments are evidences in favor of the pyramidal configuration of the molecules. There are, however, discrepancies that should be mentioned.

The usual procedure for processing the primary data of electron diffraction experiments gives interatomic distances $R_g(R-Cl)$ and bond angles $\angle_g(Cl-R-Cl)$ for an effective thermal average configuration. Temperature effects can be included by introducing vibrational corrections, that is, using a procedure for joint analysis of electron diffraction and spectral data. The structures of lanthanide trihalides obtained in this way were reported by Zasorin (1988). The reliability of these results was analyzed by Hargittai (2000). According to this author, the analysis of electron diffraction data in the harmonic approximation exaggerates the results compared with their expected values. Equilibrium values should lie between them and the data on the effective thermal average configuration. More recently, this conclusion was substantiated by Spiridonov et al. (2001). Earlier, Spiridinov et al. (1990) reported the atomic spacing (2.560 Å) and a still larger bond angle (116.5°) for $LaCl_3$ found using an improved harmonic analysis procedure.

We mention these results because Giricheva et al. (2000a,b,c,d), who studied the structures of GdCl₃, ErCl₃, TmCl₃, and LuCl₃ by electron diffraction together with a mass spectrometric analysis of their association in high-temperature vapors, give $R_g(R-Cl)$ and $\angle_g(Cl-R-Cl)$ values and claim that the thermal average configuration of these molecules is pyramidal, whereas the equilibrium configuration of GdCl₃, TmCl₃, and LuCl₃ is planar (Giricheva et al., 2000d), and that of ErCl₃, pyramidal according to (Giricheva et al., 2000d) and more recent work (Zakharov et al., 2001) concerned with the structure of ErBr₃. This is not quite logical considering the tendencies of molecular parameter variations in the series of compounds under consideration.

In order to estimate the interatomic distances in the series of lanthanide trichlorides, we described the available data on interatomic distances by a polynomial. For this purpose, we used the results obtained for LaCl₃ in Spiridinov et al. (1990) and LaCl₃, PrCl₃, GdCl₃, TbCl₃, HoCl₃, and LuCl₃ in Zasorin (1988). As far as the data from Zasorin (1988) are concerned, we used both thermal average distances and the distances obtained by this author when introducing vibrational corrections. Calculations of interatomic distances by the polynomial and their comparison with the results from Giricheva et al. (2000a,b,c,d) show that they coincide with the $R_g(R-Cl)$ values to within 0.003–0.005 Å.

As estimated from theoretical calculations (Kovács, 2000; Vetere et al., 2000), the bond angles obtained in electron diffraction studies show no definite pattern of variations characteristic of the compounds under consideration. Experimental difficulties with this class of compounds are possibly explained by their complex behavior at high temperatures, especially in melts. It can be seen from this work that the authors of both IR and electron diffraction studies currently pay much attention to molecular association. These effects can, however, be minimized under certain conditions. The outcome is that, according to Laptev et al. (1986) and Goryushkin et al. (1990b), lanthanide trichlorides can noticeably decompose starting at specific temperatures. In particular, melting is accompanied with extensive decomposition. The resulting nonstoichiometric condensed phase vaporizes incongruently, and the activity of the lanthanide trichloride drops, which causes a decrease in the partial pressure of the monomer and, therefore, a still more noticeable decrease in the saturated vapor pressure of the dimer. The decomposition of lanthanide trichlorides can be accompanied by the appearance of their dichlorides, which, according to Chervonnyi (1977a), exist for the whole series of lanthanides. It should in addition be taken into account that the material of the container from which lanthanide trichlorides are vaporized can intensify these processes. The results obtained in studying the photoelectron spectra of vapors of these compounds (Lee et al., 1982) are instructive in this respect.

The too large spread of data, even those obtained by a single research team (see, for instance, the series of works by Giricheva et al., 2000a,b,c,d or Zasorin, 1988), impedes a sound selection of a sample from the entire set of data. For instance, Zasorin (1988), who believed bond angles to increase in the series of lanthanide trichlorides, nevertheless recommended several mean values that he calculated as the being the most reliable ones for the whole series of compounds.

This constitutes an argument in favor of using theoretical bond angles (Joubert et al., 1998b; Kovács, 2000; Vetere et al., 2000) in thermodynamic function calculations. The theoretical bond angle values change from \sim 118° for LaCl₃ to \sim 120° for LuCl₃. It follows that all lanthanide trihalides except LuCl₃ have pyramidal configurations: the angle in LuCl₃ is equal to 120° according to Kovács (2000) and Vetere et al. (2000) and to 119.9° according to Joubert et al. (1998b). Nevertheless, a pyramidal geometry was experimentally found for LuCl₃ at T = 1070 K) (Giricheva et al., 2000d). It is likely that lutetium trichloride should also be considered pyramidal in thermodynamic calculations, and the angles should be selected taking into account both theoretical calculations and experimental electron diffraction data. The selected angles should conform to the general rule governing parameter variations in the series of lanthanide trihalides: the angles should comparatively rapidly increase along the series of light lanthanides and more slowly along the series of heavy lanthanides. The reliability of thermodynamic function calculations (first and foremost, for LuCl₃) should be established using the experimental data obtained in studying various equilibria with the participation of gaseous lanthanide trichlorides.

The molecular constants of lanthanide trichlorides accepted in this work are summarized in Table 1 in the form of the coefficients of polynomial (1).

P _i (n)	A _i	B _i	Ci
$v_1 ({\rm cm}^{-1})$	306.09630	2.42963	-0.02593
$v_2 ({\rm cm}^{-1})$	58.55664	0.56749	-0.01001
$v_3 ({\rm cm}^{-1})$	314.29932	3.04314	-0.05334
$v_4 ({\rm cm}^{-1})$	73.01397	1.1187	-0.00998
R(R-Cl) (Å)	2.57590	-0.01478	1.93124×10^{-4}
\angle (Cl-R-Cl) (°)	115.11429	0.29286	-0.00714

TABLE 1 Molecular constants of RCl₃(g)

2.1.5 Electronic states

Myers and Graves (1977a) have calculated thermodynamic functions which include electronic excitation contributions. They used the energies of excited electronic levels of triply charged lanthanide ions in crystals reported by Dieke (1968) and the data from Carnall et al. (1976) for Pm^{3+} . Levels situated below 5000 cm⁻¹ were taken into account, while levels above this limit were assumed to make no substantial contribution to the calculated values.

Currently, we have a refined summary of data on the energy levels of R^{3+} ions for the whole series of lanthanides except Pm^{3+} (Martin et al., 1978). This opens up the possibility of more completely calculating the electronic contributions to thermodynamic functions. We assume that precise calculations of thermodynamic functions in the temperature range 298.15–3000 K can be performed by including the central ion states whose energy does not exceed 10,000 cm⁻¹. Higher energy states make negligibly small contributions.

A much stronger effect on the values of thermodynamic functions arises from changes in the energy of low-lying central atom electronic states caused by the Stark splitting of these states in ligand fields. This splitting can be included since corresponding experimental data on lanthanide ions doped in various crystal lattices are known. In particular, such data are available for almost the whole series of lanthanide ions incorporated into the crystal field with C_{3h} symmetry of lanthanum trichloride (Morrison and Leavitt, 1982).

Global interpretation of both experimental and theoretical data on the influence of various crystal fields on the splitting of electronic states led several authors to conclude that the 4f shells of lanthanide ions are screened from direct action of the ligands by the outer 5s and 5p shells (Kaminskii, 1975; Kück, 2001; Kustov et al., 1981; Morrison, 1992). That is, experimental data can be reproduced theoretically using weak crystal field analysis. No matter which crystal field symmetry, the Stark levels are grouped around the energies that satisfactorily coincide with those of the free ions. The general features of the absorption and luminescence spectra change insignificantly in going from one crystal to another. For instance, the assignment of the transitions (without taking Stark splitting into account) suggested in Caird et al. (1981) for the absorption and emission spectra of the TbCl₃·AlCl₃ adduct molecule in the gas phase showed that the energies of the terms of Tb³⁺ in this molecule virtually coincide with those for triply charged terbium in the LaCl₃ crystal (Morrison and Leavitt, 1982). Earlier, Gruen and DeKock (1966) had studied NdBr₃ and NdI₃ and found that the substitution of the ligand only caused changes in the intensities of certain absorption bands. Later, Lin and Zollweg (1974) studied the CsNdI₄ and CsCeI₄ complex molecules in the gas phase and showed that a change in symmetry around the Nd^{3+} ion only slightly shifts the absorption bands.

The Stark splitting of levels above the ground level (as a rule, the splitting value is then larger than 1000 cm^{-1}) can be ignored in calculating the electronic component of the reduced Gibbs energy in the series of lanthanide trichlorides because its effect does not exceed 0.1 J/(mol·K). As the splitting of each of these multiplets is smaller than the energy difference between the multiplets, the calculations can be performed by using either the energy values corresponding to the centers of gravity of the multiplets (Kaminskii, 1975; Kück, 2001; Kustov et al., 1981; Morrison, 1992) or the energies of the free R³⁺ ions from Martin et al. (1978).

As far as the ground state is concerned, it is necessary to take Stark splitting into account. For example, the temperature dependence of the electronic contributions to the reduced Gibbs energy calculated by us for ErCl_3 is shown in Figure 2. The calculations were performed ignoring Stark splitting (curve 1) and on the assumption that this splitting coincided with that observed in the crystal fields of LaCl_3 (field symmetry C_{3h}) (curve 2, drawn based on the data from Morrison and Leavitt, 1982), LiYF₄ (S_4 symmetry, curve 3 based on the data from Sviridov et al., 1976),



FIGURE 2 Temperature dependences of the electronic contributions to the reduced Gibbs energy for erbium trichloride. See text for explanations. Reproduced from Chervonnyi and Chervonnaya (2004g) with permission from Pleiades Publishing, Ltd.

and LaF₃ (C_2 symmetry, curve 4 based on the data from Sviridov et al., 1976). The data on the splitting of the same Er^{3+} level in other crystal fields (Kaminskii, 1975) lead to curves that lie between curves 3 and 4 and are not shown in Figure 2.

It follows from the shape of the curves that taking into account the Stark splitting noticeably decreases the electronic contribution over the whole temperature range. This decrease is larger in the region of low temperatures for the temperature interval under consideration. In addition, curves 2–4 show that ligand field splitting depends on field symmetry and strength. Indeed, the electronic contributions have noticeably different magnitudes in different crystal fields but have similar temperature dependences. According to the data known to us, the decrease in the electronic component caused by including Stark splitting is smallest in lanthanum trichloride and probably closest to what should be observed for the ligand field splitting in gaseous molecules. This conclusion is based on two considerations.

First, comparison of, for instance, the centers of gravity of the ${}^{4}I_{9/2}$ multiplet of the Nd³⁺ ion as deduced from the ligand field splittings reported by Kaminskii (1975) for various crystal fields shows that their positions vary within $\pm 15\%$ of the mean value. Second, in both cases, the lanthanide ion is in the field of the same ligands, although the number of Cl⁻ ions that act on the lanthanide ion in the crystal is larger. In view of this, we accepted that the electronic contribution to the reduced Gibbs energy can, as a first approximation, be calculated from the data reported by Morrison and Leavitt (1982) for the energies of ligand field sublevels of the ground electronic state in order to take into account the ligand field action on the central atom. Our estimates can be refined as experimental or theoretical data describing this splitting in molecules in the gas phase will be accumulated. In addition, the reliability of thermodynamic functions (therefore, the correctness of estimates) can be checked against experimental data processed using the reduced Gibbs energies of gaseous lanthanide trichlorides.

Table 2 contains the electronic state energies and their statistical weights in RCl₃ that were included in the calculations of thermodynamic functions. Note that not all data required for the calculations can be found in the review by Morrison and Leavitt (1982). They have been augmented by data from several original papers. In particular, we refined the positions of levels and their statistical weights for Pr^{3+} and Pm^{3+} according to the data from Burdick and Richardson (1998) and Carnall et al. (1976), respectively. The energies for the ⁶H_{9/2} and ⁶F_{11/2} states of the Dy³⁺ ion were refined using the results obtained by Lorenzo et al. (1996). The spectra of the Stark splitting of the ground electronic state of the Tm³⁺ and Yb³⁺ ions were found taking into account the results obtained by

R	Ground state	Electronic state energies (cm ⁻¹) and their statistical weights (within parentheses)
La	${}^{1}S_{0}$	0(1)
Ce	${}^{2}F_{5/2}$	0(2), 37.5(2), 110(2), 2253(8)
Pr	$^{3}H_{4}$	0(2), 33.1(1), 96.4(2), 130.2(2), 137.0(1), 199.5(1), 2152.09
		(11), 4389.09(13), 4996.61(5), 6415.24(7), 6854.75(9), 9921.24(9)
Nd	${}^{4}I_{9/2}$	0(2), 115.39(2), 123.21(2), 244.4(2), 249.4(2), 1880(12), 3860(14), 5910(16)
Pm	${}^{5}I_{4}$	0(2), 66.6(2), 84.5(1), 100.1(2), 127.0(1), 240.0(1), 1490(11),
	-	3110(13), 4820(15), 6580(17)
Sm	⁶ H _{5/2}	0(2), 40.7(2), 66.1(2), 1080(8), 2290(10), 3610(12), 4990(14),
	-,	6290(2), 6470(16), 6540(4), 7050(6), 7910(8), 9080(10)
Eu	$^{7}F_{0}$	0(1), 370(3), 1040(5), 1890(7), 2860(9), 3910(11), 4940(13)
Gd	${}^{8}S_{7/2}$	0(8)
Tb	$^{7}F_{6}$	0(2), 56.83(2), 90.56(1), 97.22(2), 99.31(2), 104.64(1),
		112.80(2), 117.99(1), 2051.6(11), 3314.2(9), 4292.3(7),
		4977.9(5), 5431.8(3), 5563.8(1)
Dy	⁶ H _{15/2}	0(2), 9.82(2), 9.97(2), 15.65(2), 40.75(2), 80.48(2), 121.65(2),
	_	140.51(2), 3460(14), 5780(12), 7650(22), 8950(10), 9060(8)
Но	${}^{5}I_{8}$	0(2), 12.51(2), 43.80(1), 66.42(2), 89.92(1), 104.12(2),
		118.40(1), 154.21(1), 155.41(2), 203.69(1), 212.78(2),
		5050(15), 8550(13)
Er	${}^{4}I_{15/2}$	0(2), 37.91(2), 64.27(2), 96.52(2), 113.70(2), 114.61(2),
		181.04(2), 229.31(2), 6480(14)
Tm	$^{3}\text{H}_{6}$	0(1), 29(2), 92(2), 121(1), 127(2), 175(2), 188(1), 195(1),
	2	222(1), 5640(9), 8090(11)
Yb	$^{2}F_{7/2}$	0(2), 48(2), 127(2), 253(2)
Lu	$^{1}S_{0}$	0(1)

TABLE 2 Electronic states of R^{3+} in $RCl_3(g)$

Mujaji and Comins (1998) and Carnall et al. (1989), respectively. As the half-filled or completely filled 4f shell has an increased stability, no Stark splitting is observed for the Gd^{3+} ion in the R^{3+} series of compounds under consideration.

Figure 3 shows the difference between the Φ_{el}° values for RCl₃(g) when they are calculated with and without taking into account the Stark splitting of the ground term. As follows from the data shown in Figure 3, in some compounds under study, this difference is noticeable enough. It can reach ~5 J/(mol·K).



FIGURE 3 Difference between the Φ_{el}° values calculated with and without taking into account the Stark splitting of the ground electronic term for RCl₃(g).

2.1.6 Thermodynamic functions

The selected molecular constants and electronic state excitation energies were then used to calculate the thermodynamic functions of the 15 lanthanide trichloride molecules in the rigid rotator–harmonic oscillator approximation and in the temperature range 298.15–3000 K at standard pressure. All the necessary equations for calculating the reduced Gibbs energy were taken from the compilation by Gurvich et al. (1978–1984). Fundamental constants, including the atomic weights of lanthanides and chlorine, were taken from the NIST site and from Mohr and Taylor (1999). These data are periodically updated. The latest values of these fundamental constants can be found in Mohr et al. (2008a,b).

The resulting thermodynamic functions are collected in Table A1 in the form of the f_i coefficients (see Appendix).

When the rigid rotator–harmonic oscillator model was applied to molecules with two C_{3v} configurations separated by an energy barrier, the results obtained by Godnev (1953) were used. This author showed in

the case of NH₃ that the thermodynamic functions of molecules of this type should be calculated in the anharmonic approximation by direct summation with the symmetry number 6. Accordingly, the components of inversion splitting of the out-of-plane bending vibration (v_2) overtones can be considered as being equidistant and spaced by a value $v_2/2$, starting with $v_2 = 4$. The equations for calculations in the harmonic approximation include the symmetry number 3 and the v_2 value. Indeed, we find a difference in the values of the reduced Gibbs energy of the molecule NH₃ when calculated in the harmonic and anharmonic approximations for the out-of-plane bending vibrations. This difference lies in the interval [-1.34, +0.11] J/(mol·K) after calculating the reduced Gibbs energy in the temperature range 298.15–6000 K.

This means that for calculating the product of inertia moments, we need to consider the pyramidal configuration of the molecules.

For this reason, the detailed description of thermally averaged configurations has been performed above on the basis of electron diffraction experiments. The newest results (Giricheva et al., 2006, 2009; Lanza et al., 2008; Zakharov et al., 2004) for bond lengths and bond angles for several lanthanide trichlorides are summarized in Table 3. The molecular constants taken into account in the calculation of thermodynamic functions (Chervonnyi and Chervonnaya, 2004g) and those obtained experimentally after the publication of our data are in good agreement with each other. Although it should be noted that the absolute bond angle and bond length values introduced in the equation for calculating the product of the moments of inertia very weakly influence the values of the reduced Gibbs

	Т (К)	R _g (R—Cl) (Å)	∠ _g Cl—R—Cl (°)	<i>R</i> (R—Cl) (Å)	∠Cl—R—Cl (°)
R	Experin	nental		Reported in Chervonnaya	Chervonnyi and a (2004g)
La	1295	2.589 ^a	116.7 ^{<i>a</i>}	2.561	115.4
Sm	1205	2.511 ^b	115.6 ^b	2.494	116.6
Dy	1160	2.453 ^b	116.8 ^b	2.447	117.2
	1270	2.459 ^c	_	_	_
Ho	1148	2.444^{b}	116.6 ^b	2.437	117.3
Er	1165	2.436^{d}	117.0 ^d	2.426	117.5
Yb	1170	2.416 ^d	117.2 ^d	2.407	117.8

TABLE 3 Bond lengths and bond angles for several lanthanide trichlorides

^a Zakharov et al. (2004).

^b Giricheva et al. (2006).

^c Lanza et al. (2008).

^d Giricheva et al. (2009).

energy. Estimates show that bond angle changes from 115° to 119.8° cause reduced Gibbs energy variations by 0–0.16 J/(mol·K). In turn, increasing the bond length by 0.02 Å leads to an increase in the reduced Gibbs energy of ~0.2 J/(mol·K).

In this respect, of great importance is the comparison of the thermodynamic functions calculated in harmonic and anharmonic approaches for the out-of-plane bending vibrations (v_2) . The influence of the anharmonicity of this vibrations was recently considered by Gorokhov et al. (2002) and Gorokhov and Osina (2002). These authors based their study on the conclusions made by Solomonik and Marochko (2000a,b) and calculated the energy levels of the v_2 anharmonic vibration for LaCl₃ through solving the Schrödinger equation by the variational method with a basis set of 1200 harmonic oscillators for the potential function describing the structural nonrigidity of this compound. The contribution of this vibration to thermodynamic functions was then calculated by direct summation. At the highest temperature (3000 K), the contributions of 533 vibrational levels were summed up. The obtained reduced Gibbs energy values (open circles) are shown in Figure 4 for LaCl₃(g). For comparison, the same figure contains data from Chervonnyi and Chervonnaya (2004g) obtained in the rigid rotator-harmonic oscillator approximation (curve 1).



FIGURE 4 Reduced Gibbs energies of $LaCl_3(g)$ calculated in the harmonic and anharmonic approximations for the out-of-plane bending vibration frequency v_2 . See text for explanations.

Comparison of the results (Chervonnyi and Chervonnaya, 2004g; Gorokhov and Osina, 2002) shows that the inclusion of anharmonicity of the out-of-plane bending vibrations approximately equally changes the temperature dependences of the reduced Gibbs energy for LaCl₃. The reduced Gibbs energy becomes larger than in the harmonic approximation at low temperatures and smaller at higher temperatures. The absolute difference at the boundaries of the temperature range amounts to $\sim 2 \text{ J/(mol} \cdot \text{K})$. With such a temperature dependence of the reduced Gibbs energy in the temperature interval under consideration, the results obtained by both methods coincide at a certain temperature. In particular, this coincidence is observed for lanthanum trichloride at temperatures that are of interest for processing experimental data on various equilibria with the participation of these molecules by the third law of thermodynamics.

Differences on the same order are observed when comparing data for other RCl₃(g) computed by Gorokhov and Osina (see Kudin, 2002) with the results of our calculation in the harmonic approximation (Chervonnyi and Chervonnaya, 2004g). The differences in the values of the reduced Gibbs energy for T = 1000 K are -0.622 (PrCl₃), -0.276 (NdCl₃), -0.028 (PmCl₃), +1.462 (EuCl₃), +2.022 (GdCl₃), +0.939 (TbCl₃), +1.446 (DyCl₃), +0.942 (HoCl₃), +1.365 (ErCl₃), +1.374 (TmCl₃), and +1.829 (YbCl₃) J/(mol·K). The same difference is equal to -0.391 J/(mol·K) for LaCl₃ (see Figure 4). The size of this difference (in % from the - [$G^{\circ}(T) - H^{\circ}(0)$]/T value) lies in the interval [-0.10, +0.51] for the entire RCl₃(g) series.

It should be noted that another approach was also used in the calculation of electronic contributions to the reduced Gibbs energy by Gorokhov and Osina (see Kudin, 2002). In this work, the electronic contribution for RCl₃ was estimated in some cases by using the energies obtained from *ab initio* calculations (Tsuchia et al., 1999) for the corresponding monomers (CeCl₃, PrCl₃, SmCl₃, EuCl₃, TbCl₃, and YbCl₃). For the other RCl₃ molecules (R = Nd, Pm, Dy, Ho, Er, and Tm), only the data of Morrison and Leavitt (1982) on the splitting of the ground electronic state of R³⁺ were taken into account. In all cases, the energies of relatively high-lying states (up to 10,000 cm⁻¹) were taken from (Martin et al., 1978).

Recently, full sets of molecular constants have been published by Kovács and Konings (2004) for $RX_3(g)$ (where X = F, Cl, Br, I). The stretching and bending vibration frequencies and internuclear distances accepted in this work differ from the estimates by Kovács and Konings (2004) by ~4 cm⁻¹, ~10 cm⁻¹, and ~0.02 Å, respectively. Calculation of the reduced Gibbs energy using molecular constants from Kovács and Konings (2004) gave results which are smaller by ~2–2.5 J/(mol·K) in the whole temperature range, see curve 2 in Figure 4.

Because of the difference in the symmetry number and refined calculations of electronic excitation energies, the reduced Gibbs energy values obtained by Myers and Graves (1977a) are lower by \sim 4–6 J/(mol·K) for

the whole series of lanthanide trichlorides (see curve 3 in Figure 4). Use of structural parameters for planar configuration is an incorrect procedure of calculation in the harmonic approximation for structurally nonrigid molecules.

Recently, Hargittai (2009a,b) described the structural characteristics of metal halides, including nonrigid "floppy" molecules, and analyzed the influence of these features on the experimental and calculated molecular parameters. However, the above examples show that the molecular constants provided in the calculation of the thermodynamic functions in the harmonic approximation led to sufficient accurate results for their subsequent use in practical modeling of the thermodynamic equilibria (Chervonnyi and Chervonnaya, 2004g).

2.2 Thermodynamic functions for lanthanide trifluoride molecules

The data reported by Myers and Graves (1977a) cannot be used in thermodynamic calculations for two reasons. First, both molecular parameters of the molecules in the gas phase and the electronic excitation contribution, in particular the one arising from the Stark splitting of the ground-state levels, should be revised. Second, calculations were performed with the symmetry number equal to 6, whereas the symmetry number should be set equal to 3. This is substantiated in detail in Chervonnyi and Chervonnaya (2004g), in which calculations of the thermodynamic functions for lanthanide trichlorides in the gaseous state were performed.

In calculating the thermodynamic functions for lanthanide fluorides in the gas phase, RF₃(g), we did not analyze the molecular constants and used the data from Kovács and Konings (2004) reproduced in Table 4 in the form of the coefficients of the polynomial (1) (Chervonnyi and Chervonnaya, 2007a).

P _i (n)	A _i	B _i	C _i
$v_1 (cm^{-1})$	528.0	4.0	0
$v_2 ({\rm cm}^{-1})$	77.46593	1.79690	-0.00695
$v_3 (cm^{-1})$	496.2	4.90735	0.00735
$v_4 ({\rm cm}^{-1})$	121.57143	1.67857	-5.55112×10^{-17}
R(R-Cl) (Å)	2.08688	-0.00958	-7.27214×10^{-7}
\angle (Cl-R-Cl) (°)	108.5	0.5	0

TABLE 4 Molecular constants in RF₃(g) according to Kovács and Konings (2004)

We accepted that the electronic component of the reduced Gibbs energy can be calculated from the data reported by Morrison and Leavitt (1982) for the splitting energies of the ground electronic state of triply charged lanthanide ions in the LaF₃ crystal field. Additionally, we refined the positions of levels and their statistical weights for Pm^{3+} according to the data from Carnall et al. (1976, 1977). In all cases, the energies of relatively high-lying states (up to 10,000 cm⁻¹) were taken from Martin et al. (1978). The electronic state energies and their statistical weights that were included in calculations of thermodynamic functions for RF₃(g) are listed in Table 5.

R	Ground state	Electronic state energies (cm ⁻¹) and their statistical weights (within parentheses)
La	${}^{1}S_{0}$	0(1)
Ce	$^{2}F_{5/2}$	0(2), 151(2), 280(2), 2160(2), 2240(2), 2635(2), 2845(2)
Pr	$^{3}H_{4}$	0(1), 59.7(1), 69.4(1), 134.7(1), 202.4(1), 222.6(1), 290.4(1), 330.7(1), 500.1(1), 2152.09(11), 4389.09(13), 4996.61(5), 6415.24(7), 6854.75(9), 9921.24(9)
Nd	${}^{4}I_{9/2}$	0(2), 45(2), 136(2), 296(2), 500(2), 1978(2), 2037(2), 2068(2), 2091(2), 2187(2), 2223(2), 3860(14), 5910(16)
Pm	${}^{5}I_{4}$	0(2), 91(2), 116(1), 138(2), 175(1), 331(1), 1612(11), 3239(13), 4951(15), 6714(17)
Sm	⁶ H _{5/2}	0(2), 44.5(2), 159.4(2), 1003.4(2), 1047.0(2), 1100.6(2), 1187.0(2), 2290(10), 3610(12), 4990(14), 6290(2), 6470(16), 6540(4), 7050(6), 7910(8), 9080(10)
Eu	⁷ F ₀	0(1), 313(1), 375(1), 415(1), 946(2), 997(2), 1098(1), 1890(7), 2860(9), 3910(11), 4940(13)
Gd	${}^{8}S_{7/2}$	0(8)
Tb	${}^{7}F_{6}$	0(1), 42(1), 60(1), 125(1), 140(1), 169(1), 209(1), 212(1), 217(1), 232(1), 319(1), 353(1), 488(1), 2051.6(11), 3314.2(9), 4292.3(7), 4977.9(5), 5431.8(3), 5563.8(1)
Dy	⁶ H _{15/2}	0(2), 42.3(2), 61.8(2), 110.9(2), 154.9(2), 210.7(2), 272.3(2), 468.5(2), 3460(14), 5780(12), 7650(22), 8950(10), 9060(8)
Но	⁵ I ₈	0(2), 7.3(2), 18.7(1), 32.5(2), 54.1(1), 76.7(2), 103.5(1), 125.3(1), 149.4(2), 204.2(1), 211.1(2), 5050(15), 8550(13)
Er	${}^{4}I_{15/2}$	0(2), 52.0(2), 64.3(2), 96.5(2), 113.7(2), 114.6(2), 181.0(2), 229.3(2), 6480(14)
Tm	³ H ₆	0(1), 67(1), 118(1), 156(1), 204(1), 235(1), 272(1), 274(1), 349(1), 354(1), 400(1), 415(1), 441(1), 5640(9), 8090(11)
Yb	$^{2}F_{7/2}$	0(2), 78(2), 185(2), 401(2)
Lu	${}^{1}S_{0}$	0(1)

TABLE 5 Electronic states of R^{3+} in $RF_3(g)$

The selected molecular constants and electronic state excitation energies were used to calculate the thermodynamic functions in the rigid rotator–harmonic oscillator approximation over the temperature range 298.15–3000 K at standard pressure. These functions are gathered in Table A2 in the form of the f_i coefficients of the polynomial (see Appendix).

For these calculations, molecular constants were estimated from the experimental data selected based on their internal consistency within the series of lanthanide fluorides. Accordingly, we think that the following errors may be estimated: ± 0.01 Å for atomic spacings, ± 5 cm⁻¹ for vibrational frequencies, and $\pm 2^{\circ}$ for bond angles. An additional uncertainty is introduced into Φ_{el}° values by errors in electronic excitation energies and the neglect of anharmonicity of the v_2 vibrations. However, the overall error in reduced Gibbs energies does not exceed ± 3 J/(mol·K).

3. THERMODYNAMIC FUNCTIONS FOR LANTHANIDE DIHALIDE MOLECULES

3.1 Thermodynamic functions for lanthanide dichloride molecules

Lanthanide chlorides exhibit a tendency toward a decrease in the stability of the higher valence states of the central atom in the gas phase compared with the condensed state. For instance, RCl_3 form in the condensed state for all lanthanides, but only some of them (Sm, Eu, and Yb) form dichlorides with compositions close to a 1:2 stoichiometriy. In the gas phase, chlorides in which lanthanides have oxidation states +1, +2, and +3 have been identified. At the same time, it follows from several independent studies that gaseous europium trichloride is fairly problematic to detect.

The existence of SmCl₂, EuCl₂, and YbCl₂ in the gas phase was proved by various methods, including mass spectrometry (Chervonnyi, 1977a; Hariharan et al., 1972; Hastie et al., 1968), IR spectroscopy (Beattie et al., 1983; DeKock et al., 1972; Hastie et al., 1971; Loktyushina et al., 1984), and photoelectron spectroscopy (Lee et al., 1982). As far as the other lanthanide dichlorides are concerned, their appearance in saturated vapors was established for the whole series of lanthanides, except lanthanum and promethium, by mass spectrometric studies (Chervonnyi, 1977a; Chervonnyi and Chervonnaya, 2004b) of the products of the exchange reactions $EuCl_2(g) + R(g)$ or $BaCl_2(g) + R(g)$. More recently, the formation of these compounds was substantiated by the IR spectra of the products formed in the interaction between metallic Eu, Gd, Ho, and Yb with chlorine (Loktyushina et al., 1984). Note that, according to the results obtained by Chervonnyi and Chervonnaya (2004a, 2005b), chlorides of lanthanides in various oxidation states simultaneously appear in saturated vapors under reducing conditions. Moreover, it was shown that, even in a neutral medium, the saturated vapor composition was complex. This follows from calculations of the composition of saturated vapor over europium di- and trichlorides based on an analysis of the thermodynamic properties of europium di- and trichlorides both in condensed and in gaseous phases and of EuCl in gas phase (Chervonnyi and Chervonnaya, 2004a, 2005b). Saturated vapor can contain variable-valence europium chlorides, atomic and molecular chlorine, and atomic europium depending on temperature and on the composition of the condensed phase. Determination of the thermodynamic functions for the compounds under consideration is obviously time consuming because thermodynamic calculations of equilibria for reactions with the participation of gaseous lanthanide chlorides (including RCl₂) are frequently necessary.

The thermodynamic functions for lanthanide dichlorides in the ideal gas state have been calculated within the rigid rotator-harmonic oscillator approximation for EuCl₂ (Hariharan and Eick, 1972), YbCl₂ (Hariharan et al., 1972), and the whole series of lanthanide dichlorides (Chervonnyi, 1973). In the latter work, the necessary molecular constants (vibrational frequencies, \angle (Cl-R-Cl) angle values, and interatomic distances) were estimated from a limited number of experimental data on three lanthanide dichlorides only (SmCl₂, EuCl₂, and YbCl₂). More recently, some new data were collected for these parameters, the range of the studied compounds was extended, and uncertainty in the assignment of some IR bands was lifted. These refinements, however, weakly influence the thermodynamic properties of the compounds under consideration. In reality, the monotonic character of variations in, for example, the reduced Gibbs energy $- [G^{\circ}(T) - H^{\circ}(0)]/T$, along the series of similar lanthanide compounds, is disturbed when excited electronic states are included. This is the main reason why we undertook new calculations of the thermodynamic properties (Chervonnyi and Chervonnaya, 2003, 2004c). The matter is that earlier results (Chervonnyi, 1973; Hariharan et al., 1972; Hariharan and Eick, 1972) were obtained by taking into account the ground electronic state of RCl₂ molecules only. At present, there available data (Martin et al., 1978) allow us to perform more correct calculations of the electronic contribution to thermodynamic functions. But it was necessary to unravel characteristic tendencies for divalent lanthanide compounds that might be used for obtaining sound estimates of the Stark splitting of the ground electronic states of the central atom.

3.1.1 Molecular constants

The first experimental determination of the molecular constants of RCl_2 was performed in two independent IR studies on $SmCl_2$ (DeKock et al., 1972), EuCl₂ (DeKock et al., 1972; Hastie et al., 1971), and YbCl₂ (DeKock

et al., 1972) published within a short span of time. The spectra were recorded for matrix-isolated substances in Ne, Ar, Kr, and N₂ at \sim 20 K. These molecular constants were used in the calculations of the thermodynamic functions for lanthanide dichlorides reported by Hariharan et al. (1972), Hariharan and Eick (1972), and Chervonnyi (1973). The IR spectrum of YbCl₂ was reinvestigated later by Beattie et al. (1983), and the IR spectra of the products of the interaction between atomic Eu, Gd, Ho, and Yb with molecular chlorine in a very dilute argon matrix were recorded by Loktyushina et al. (1984).

A comparative analysis of the results published by several authors (Beattie et al., 1983; DeKock et al., 1972; Hastie et al., 1971; Loktyushina et al., 1984) yields information about the vibrational frequencies of RCl₂ in addition to those published by DeKock et al. (1972) and Loktyushina et al. (1984). The first authors assumed that the frequencies measured in an argon matrix are closest to the true frequencies of gaseous RCl₂ molecules. Unfortunately, the corresponding IR spectra were not reported in (DeKock et al., 1972), but it was pointed out that they contained some split bands (271.5 and 276 cm⁻¹ for SmCl₂, 271.5 and 276 cm⁻¹ for EuCl₂, and 282 and 286 cm⁻¹ for YbCl₂). Similar pairs of bands, naturally shifted in frequency, were also observed in krypton matrices but not in nitrogen matrices. The authors, nevertheless, believe these bands to arise from intrinsic matrix effects and that they mask the v_1 vibrational mode. This matrix effect is absent in the spectrum of EuCl₂ (Hastie et al., 1971), and the observed singlet at 270 cm⁻¹ in an argon matrix is assigned to *v*₁. This value is close to the low-frequency doublet component (DeKock et al., 1972). We therefore assume that the frequencies 271.5 (SmCl₂), 271.5 (EuCl₂), and 282 cm⁻¹ (YbCl₂) correspond to the v_1 vibration of these lanthanide dichlorides.

A study (Loktyushina et al., 1984) of the vibrational spectra of the products of reaction of atomic Eu, Gd, Ho, and Yb with Cl₂ showed them to contain RCl₂ and RCl₃ molecules. Lanthanide dichloride molecules were predominantly formed in reactions with Eu and Yb. The formation of trichloride was characteristic of Gd. The reaction of holmium with chlorine might go in either direction depending on the initial conditions. Indeed, it was shown by Loktyushina et al. (1987) that the bands corresponding to holmium mono- and dichlorides were absent in the IR spectrum of HoCl₃.

Earlier, the same authors interpreted the spectra by correlating some bands with v_1 and v_3 vibrations of lanthanide dichlorides (Loktyushina et al., 1984). However, the low- and high-frequency bands of the triplet observed in the range 270–290 cm⁻¹ were not assigned to v_1 and v_3 in the spectrum of the products formed from molecular chlorine and atomic gadolinium. As gadolinium dichloride might form in this reaction under the conditions of IR spectrum measurements (Chervonnyi, 1977a), we treat the 270–290 cm⁻¹ band as a triplet recorded under low-resolution conditions. The low- and high-frequency shoulders of this band correspond to v_1 (273.4 cm⁻¹) and v_3 (286.1 cm⁻¹) vibrations of the GdCl₂ molecule.

The v_1 and v_3 frequencies of RCl₂ recorded in argon matrices are fairly accurately described by the second-order polynomial (see Eq. (1)).

The literature data on v_2 bending vibration frequencies of RCl₂ are less clear-cut. Only Hastie et al. (1971) were able to record the corresponding band in a krypton matrix by increasing the concentration of EuCl₂. According to both Hastie et al. (1971) and DeKock et al. (1972), v_2 does not vary much within the series of lanthanide dichlorides; the authors of these works assign the band at 64 cm⁻¹ to bending vibrations of SmCl₂ and YbCl₂. It was further assumed that the ratios v_3/v_2 and v_1/v_2 remain constant and equal to their values for EuCl₂ over the whole series of lanthanide dichlorides, which allowed us to calculate v_2 for all these compounds. As a result, we obtained the dependence of v_2 on the number of the lanthanide in the series. Note that the validity of this approach to calculating bending vibration frequencies is substantiated by the behavior of the v_3/v_1 ratio. If experimental data are treated properly, this ratio remains constant.

The isotopic splitting of the v_3 band (Beattie et al., 1983; DeKock et al., 1972; Hastie et al., 1971) and of the v_1 band (Beattie, 1999; Hastie et al., 1971) gives reasons to consider RCl₂ as being bent molecules. Estimative calculations give \angle (Cl-Sm-Cl) = 130 \pm 15° (Hastie et al., 1971), \angle (Cl-Eu-Cl) = 135 \pm 15° (Hastie et al., 1971), \angle (Cl-Eu-Cl) = 135 \pm 15° (Hastie et al., 1971), \angle (Cl-Eu-Cl) = 130 \pm 15° (DeKock et al., 1972), \angle (Cl-Yb-Cl) = 140 \pm 15° (DeKock et al., 1972), and \angle (Cl-Yb-Cl) = 126 \pm 5° (Beattie, 1999; Beattie et al., 1983).

More accurate angle values were obtained later by analyzing electron diffraction data (Zasorin et al., 1992). Four angle values are listed for each compound. The $\angle_{g}(Cl-R-Cl)$ angles were obtained by routinely processing electron diffraction patterns and characterize the mean configurations of the dichlorides. The $\angle_{e}^{h}(Cl-R-Cl)$ and $\angle_{e}^{ch}(Cl-R-Cl)$ angles were calculated using various harmonic analysis techniques (Spiridonov et al., 2001), the first of which overestimates angle values (Hargittai, 2000; Spiridonov et al., 2001), while the second may underestimate them (Spiridonov et al., 2001). The true angle values must lie between these estimates. Judging from the values presented in (Zasorin et al., 1992), they are close to the equilibrium $\angle_{e}(Cl-R-Cl)$ values ($\angle_{e}(Cl-Sm-Cl) = 135.9 \pm 4.2^{\circ}$, $\angle_{e}(Cl-Eu-Cl) = 136.5 \pm 4.2^{\circ}$, $\angle_{e}(Cl-Yb-Cl) = 130.2 \pm 3.6^{\circ}$), which the authors were able to obtain and which are unavailable for lanthanide trichlorides (Zasorin, 1988).

The equilibrium $\angle_{e}(Cl-R-Cl)$ values nevertheless do not fit into monotonic dependences with respect to the number of the lanthanide in the series and reflecting the lanthanide contraction, such as those found

for vibrational frequencies. According to Zasorin et al. (1992) themselves, they were unable to reliably determine the bond angle in YbCl₂ because of the limited range of scattering angles within which the electron diffraction pattern was recorded. For this reason, we ignored this value in our estimates, and angle variations were described by a linear dependence on lanthanide atomic numbers, including the angle values obtained by Zasorin et al. (1992) for SmCl₂ and EuCl₂. The estimates obtained by Hastie et al. (1971) for EuCl₂ and DeKock et al. (1972) for YbCl₂ are closest to the angle values calculated by this dependence and differ from them to within 0.7– 1.5° .

Note that linearization of the dependence of the bond angle on the lanthanide number in the series does not quite accurately reproduce changes in this parameter. The introduced error may be unimportant because angle values introduced in the equation for calculating the product of the moments of inertia very weakly influence the final reduced Gibbs energy values. Estimates show that a change in the bond angle within $\pm 1^{\circ}$ causes a change in the reduced Gibbs energy within $\pm 0.15 \text{ J/(mol·K)}$.

For the reasons specified above, we did not directly use the data of Zasorin et al. (1992) on the equilibrium interatomic distance R_e . This molecular constant was estimated from the interatomic distances in lanthanide trichlorides selected by critically analyzing the available electron diffraction data (Chervonnyi and Chervonnaya, 2004g). If the bond lengths of lanthanide trichlorides are assumed to be shorter than those of dichlorides by 0.084 Å, the curve of the interatomic distances in the latter passes between the values reported by Zasorin et al. (1992). This curve, however, more accurately reflects the lanthanide contraction in the series. Usually, molecular parameters change comparatively rapidly from La through Gd and more slowly from Gd through Lu. The interatomic distances in RCl₂ described by the corresponding polynomial are listed in Table 6.

P _i (n)	A _i	B _i	Ci
$v_1 ({\rm cm}^{-1})$	251.68989	3.50048	-0.09831
$v_2 ({\rm cm}^{-1})$	59.72213	0.74485	-0.01910
$v_3 ({\rm cm}^{-1})$	265.11011	3.30643	-0.08478
R(R-Cl) (Å)	2.65967	-0.01474	1.91257×10^{-4}
\angle (Cl-R-Cl) (°)	132.3	0.6	0

TABLE 6 Molecular constants of RCl₂(g)

3.1.2 Electronic states

In the absence of additional data, thermodynamic functions are usually calculated for the ground state of the central atom. For instance, for the compounds under consideration, the electronic contribution to the reduced thermodynamic potential was calculated as $\Phi_{el}^{\circ} = R \ln P_{xr}$ where P_x is the statistical weight of the ground electronic state of the R²⁺ ion (Chervonnyi, 1973; Hariharan and Eick, 1972; Hariharan et al., 1972). Since then, a detailed summary of R²⁺ ion electronic state energies has been published for all lanthanides except Pm²⁺ and Dy²⁺ (Martin et al., 1978). As with lanthanide trichlorides (Chervonnyi and Chervonnaya, 2004g), the thermodynamic properties of lanthanide dichlorides in the temperature range 298.15–3000 K can be calculated taking into account the electronic states of the central atom whose energy does not exceed 10,000 cm⁻¹. The higher energy states make negligibly small contributions.

The absence of data for the electronic state energies for Pm^{2+} and Dy^{2+} and the necessity of including Stark splitting of the low-energy electronic states of the central atom, prompted us to look for tendencies characteristic of divalent lanthanide compounds that might be used for obtaining sound estimates of the lacking data.

In this respect, of great importance is the circumstance mentioned in (Campos et al., 2000; Kück, 2001; Peijel et al., 2005; Rubio, 1991). When we consider the entire lanthanide series, we observe a correlation between the energy levels of the R_n^{2+} and isoelectronic R_{n+1}^{3+} ions (here, n = 1-15 is the lanthanide number in the series). We checked the data reported by Martin et al. (1978) (see Figure 5) to find out that not only the excitation energies of similar terms of the doubly charged ions are lower than the corresponding energies for isoelectronic triply charged ions but also the ratio between these energies in the pairs Ce³⁺/La²⁺, Pr³⁺/Ce²⁺, Nd³⁺/Pr²⁺, Pm³⁺/Nd²⁺, Dy³⁺/Tb²⁺, Er³⁺/Ho²⁺, Tm³⁺/Er²⁺, and Yb³⁺/Tm²⁺ is fairly accurately described by the second-order polynomial

$$\frac{E(\mathbf{R}_{n+1}^{3+})}{E(\mathbf{R}_{n}^{2+})} = 1.46123 - 0.04382n + 0.00159n^2$$
(2)

and lies in the interval 1.419–1.160. This correlation was used to estimate the energies of the excited electronic states of Pm^{2+} and Dy^2 absent in Martin et al. (1978).

The question of why the Stark splitting of high-energy R^{3+} states can and that of the ground state cannot be ignored has already been discussed in the case of gaseous lanthanide trichlorides (see Section 2). Similar arguments remain valid for gaseous lanthanide dichlorides. We were able to include Stark splitting for R^{3+} thanks to the availability of many experimental data reported for virtually all lanthanides in crystal fields of various symmetries. The situation for RCl₂ is, however, less favorable.



FIGURE 5 Ratio between the excitation energies of the analogous terms in the pairs R_{n+1}^{3+}/R_n^{2+} .

The matter is that the lanthanide ions in the trivalent state exhibit strong propensity for being incorporated into crystals. Obtaining the divalent state requires R^{3+} ions to be reduced. The divalent ions obtained in crystals in sufficient concentrations include Sm^{2+} , Eu^{2+} , Tm^{2+} , and Yb^{2+} (Grenet et al., 1980; Kiss, 1962; Kiss and Weakliem, 1965; Kück, 2001; Meijerink and Dirksen, 1995; Rubio, 1991; Wenger et al., 2001). The other R^{2+} ions are much more difficult to prepare, although studies of the Ce^{2+} , Dy^{2+} , and Ho^{2+} ions incorporated in crystals have been reported in several works (Alig et al., 1969; Kiss, 1965; Kiss et al., 1965; Weakliem and Kiss, 1967).

Because of the complete absence of literature data on the Stark splitting of the ground electronic state for gaseous lanthanide dichlorides and the deficiency of such data on R^{2+} ions in crystals, we had to estimate this splitting using the correlations described above. For this purpose, we used polynomial (2) and the Stark splitting values accepted for RCl₃ groundstate multiplets. This approach was applied to estimate the Stark splitting of the ground state of Ce²⁺, Pr²⁺, Nd²⁺, Pm²⁺, Tb²⁺, Dy²⁺, Ho²⁺, Er²⁺, and Tm²⁺. This procedure was not applied to estimate the splitting of the ground level in La²⁺ and Gd²⁺ because the configurations of their ground states did not coincide with those of the corresponding states of the Ce³⁺ and Tb³⁺ isoelectronic ions. Finally, there is no Stark splitting of the ground states of Sm²⁺, Eu²⁺, Yb²⁺, and Lu²⁺.

R	Ground state	Electronic state energies (cm ⁻¹) and their statistical weights (within parentheses)
La	$^{2}D_{3/2}$	0(4), 1603.23(6), 7195.14(6), 8695.41(8)
Ce	${}^{3}H_{4}$	0(2), 24(1), 70(2), 94(2), 99(1), 145(1), 1528.32(11), 3127.10 (13), 3276.66(9), 3762.75(5), 3821.53(5), 4764.76(7), 5006.06(9), 5127.27(9), 5502.37(7), 6265.21(7), 6361.27
		(11), 6571.36(5), 7150.05(9), 7120.00(9), 7836.72(9), 8349.99(13), 8922.05(2), 9325.51(11), 9900.49(5)
Pr	${}^{4}I_{9/2}$	0(2), 86(2), 92(2), 182(2), 186(2), 1398.34(12), 2893.14(14), 4453.76(16), 9370.66(4)
Nd	$^{5}I_{4}$	0(2), 51(2), 64(1), 76(2), 97(1), 183(1), 1137.8(11), 2387.6(13), 3714.9(15), 5093.3(17)
Pm	⁶ H _{5/2}	0(2), 32(2), 52(2), 843(8), 1786(10), 2816(12), 3893(14), 4907(2), 5047(16), 5102(4), 5500(6), 6171(8), 7083(10)
Sm	⁷ F ₀	0(1), 293.45(3), 813.55(5), 1492.66(7), 2277.88(9), 3131.54(11), 4026.99(13)
Eu	$8S_{7/2}$	0(8)
Gd	⁹ D ₂	0(5), 279.32(7), 694.37(9), 1310.13(11), 2282.83(13), 2381.24 (13), 3996.71(11), 5015.20(9), 5789.97(7), 6334.17(5), 9195.04(9), 9356.30(11), 9717.70(9)
Tb	⁶ H _{15/2}	0(2), 8(4), 13(2), 34(2), 67(2), 102(2), 118(2), 2804.67(14), 4734.52(12), 6258.08(10), 6470.11(12), 7422.21(8), 7621.556(10), 8285.885(6), 8972.29(14), 9144.98(8), 9218 63(12), 9275 42(16)
Dy	⁵ I ₈	0(2), 11(2), 37(1), 56(2), 76(1), 88(2), 100(1), 130(1), 131(2), 172(1), 180(2), 4272(15), 7233(13)
Но	${}^{4}I_{15/2}$	0(2), 32(2), 55(2), 82(2), 97(2), 98(2), 155(2), 196(2), 5438.53(14), 8644.59(12)
Er	³ H ₆	0(1), 25(2), 79(2), 104(1), 109(2), 150(2), 161(1), 167(1), 191(1), 5081.79(9), 6969.78(11)
Tm	$^{2}F_{7/2}$	0(2), 41(2), 109(2), 218(2), 8774.02(6)
Yb	${}^{1}S_{0}$	0(1)
Lu	$^{2}S_{1/2}$	0(2), 5707.6(4), 8647.8(6)

TABLE 7 Electronic states of R^{2+} in $RCl_2(g)$

Table 7 contains the energies of electronic states and their statistical weights for gaseous RCl_2 molecules used in the calculations of thermodynamic functions.

Available literature data allow us to draw conclusions about the reliability of such calculations. For instance, it follows from the experimental data and calculation results reported by Weakliem and Kiss (1967) that the center of gravity of the ${}^{4}I_{15/2}$ multiplet of Ho^{2+} incorporated into the SrCl₂ crystal is 87.4 cm⁻¹. Table 7 gives 89.4 cm⁻¹ for this value. One more example: according to the assignment of the lines corresponding to the ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition in the absorption spectrum of Tm²⁺ incorporated into the crystal field of SrCl₂ (Wenger et al., 2001), the center of gravity of the ${}^{2}F_{7/2}$ multiplet is ~ 88 cm⁻¹; Table 7 gives a value larger by 3 cm⁻¹.

The temperature dependence of the difference between Φ_{el}° values for RCl₂(g) calculated with and without taking into account the Stark splitting of the ground term is shown in Figure 6. As follows from these data, this difference is noticeable enough in some compounds under study: it can reach ~4 J/(mol·K).

The scheme used in this work for estimating Stark splittings is an approximation. Our estimates can be refined as experimental or theoretical data on this splitting in gaseous molecules will be available. In addition, the use of thermodynamic functions in the treatment of experimental data on various equilibria with the participation of gaseous lanthanide dichlorides will allow to improve the reliability of these functions and, therefore, the correctness of our estimates to be tested independently.



FIGURE 6 Difference between Φ_{el}° values calculated with and without taking into account the Stark splitting of the ground term of $RCl_2(g)$.

Analysis of the structural data for the molecules under consideration shows that the amount of such data is sufficient for reliably estimating molecular constants. Although they were obtained by different authors using different methods, they virtually do not include values whose reliability is questionable because of their substantial deviations from monotonic dependences.

3.1.3 Thermodynamic functions

The selected molecular constant values and electronic state excitation energies were used to calculate the thermodynamic functions of RCl₂ in the rigid rotator–harmonic oscillator approximation for the ideal gas state in the temperature range 298.15–3000 K at standard pressure. These functions are presented in Table A3 in the form of the f_i coefficients (see Appendix).

3.2 Thermodynamic functions for lanthanide difluoride molecules

In 2007, we carried out a systematic description of the molecular constants of this series of compounds and calculated the reduced Gibbs energy (Chervonnyi and Chervonnaya, 2007c). Previously, the thermodynamic functions were known only for LaF₂ (Hildenbrand and Lau, 1995; Krasnov and Danilova, 1969). The procedure used for selecting molecular constants and the method of calculating the excitation energies of individual electronic states of ions R^{2+} are described below.

3.2.1 Molecular constants

Molecular constants (vibration frequencies, bond lengths, bond angles) for LaF₂ used in the calculations (Hildenbrand and Lau, 1995; Krasnov and Danilova, 1969) were estimated by comparative methods. Given that the initially accepted interatomic distance ($R_e(R-F) = 2.18$ Å) is retained, the estimates by Krasnov and Timoshinin (1969), Filippenko et al. (1972), and Hildenbrand and Lau (1995) have led to different (decreasing) values for the vibrational frequencies: 594.3, 194.1, and 619.4 cm⁻¹ (Krasnov and Timoshinin, 1969); 539, 177, and 561 cm⁻¹ (Krasnov and Danilova, 1969); 500, 100, and 450 cm⁻¹ (Hildenbrand and Lau, 1995). The bond angle recommended in the first two studies is 110° (Krasnov and Danilova, 1969; Krasnov and Timoshinin, 1969), while it amounts to 140° in the last work (Hildenbrand and Lau, 1995).

Jia (1990) has described the molecular constants of RX_2 (R = La–Lu; X = F, Cl, Br, I) by taking into account the data reported by Krasnov and Timoshinin (1969), the molecular characteristics of samarium, europium, and ytterbium dichlorides and difluorides obtained from their IR spectra (DeKock et al., 1972; Hastie et al., 1971), as well as estimates by Filippenko

et al. (1972) of the interatomic distances and bond angles in europium and ytterbium dichlorides and difluorides ($R_e(Eu-F) = 2.10$ and 1.95 Å for EuF_2 and YbF₂, respectively, and $\angle_e(F-Yb-F) = 110^\circ$). The bond lengths and bond angles were calculated using empirical formulas, and then the effective nuclear charge model (Ohwada, 1980) was used for evaluating the force constants: f_r (stretching), f_{rr} (bond–bond interaction), and f_{α} (bending). From the bond angles and force constants, the fundamental frequencies were calculated in the valence force field approximation (Jia, 1990).

It would seem rational that the availability of the molecular constants for lanthanide dihalides determined by Jia (1990), while the experimental data describing their structures and vibrational frequencies are rather meager, would dictate the choice of initial data for calculating thermodynamic functions. However, it is worth noting that the use of Ohwada's model (1980) leads to a relatively high bending force constant and the calculated vibrational frequencies are at variance with the trends in their change along the lanthanide series. Indeed, the symmetric and asymmetric stretching vibration frequencies (v_1 and v_3 , respectively) increase in going from lanthanum to lutetium compounds, whereas the bending vibration frequency (v_2) decreases, although it should change in the same way as the stretching vibration frequencies.

The adequacy of the description of force constants by means of Ohwada's model was questioned by Ezhov (1992), and his doubts were confirmed when the molecular parameters of NdI_2 (Ezhov and Sevast'yanov, 2001) and $SmBr_2$ (Ezhov and Sevast'yanov, 2004) were described.

In this context, we reevaluated here the molecular constants of RF_2 for the entire lanthanide series by the procedures used for estimating analogous parameters of RCl_2 and RCl_3 . In these works, we showed that, for similar lanthanide compounds, the molecular parameters are described with high accuracy by the polynomial (1). This relationship, which reflects the effect of lanthanide contraction, can be used for estimating missing values from a small number of available data.

Our estimates are based on the results of studies on samarium, europium, and ytterbium difluorides (DeKock et al., 1972; Hastie et al., 1971), as well as on the molecular constants for RF₃ reported by Kovács and Konings (2004).

The full set of molecular constants is available only for EuF_2 (Hastie et al., 1971). These data were obtained from the IR spectrum of this compound isolated in different matrices (Ar, Ne, and N₂) at ~20 K. The v_2 frequency was detected in nitrogen and neon matrices (114.5 and 113 cm⁻¹, respectively). In addition, it was assumed that the vibrational frequencies measured in the argon matrix are the closest to the vibration frequencies of gaseous molecules. In this context, the stretching vibrational frequencies were corrected for the matrix shift (+29 cm⁻¹), which

allowed Hastie et al. (1971) to determine all vibrational frequencies ($v_1 = 487 \pm 10$, $v_2 = 114 \pm 5$, and $v_3 = 464 \pm 10 \text{ cm}^{-1}$), as well as the bond angle $\angle_{\text{e}}(\text{F}-\text{Eu}-\text{F}) = 110 \pm 15^{\circ}$ and the bond length R_{e} ($R_{\text{e}} = 2.20 \pm 0.05 \text{ Å}$) of EuF₂.

Under analogous conditions, the molecular constants of three lanthanide difluorides have been studied. The IR spectra of SmF₂, EuF₂, and YbF₂ in nitrogen and argon matrices have been reported by DeKock et al. (1972). The v_1 and v_3 values for EuF₂ coincide with those found by Hastie et al. (1971); however, the v_2 frequency was not detected for any of these compounds (DeKock et al., 1972; Hastie et al., 1971). On the other hand, scrutiny of the available data (DeKock et al., 1972; Hastie et al., 1971) shows that the experimental values of v_1 and v_3 for the above three difluorides typically depend on the lanthanide atomic number, which makes it possible to assess unknown frequencies by interpolation.

In the present assessment, we took into account the following fact: it follows from the vibrational frequencies of the RCl₃ and RCl₂ molecules (Chervonnyi and Chervonnaya, 2003, 2004g) that the $v_1(\text{RCl}_3)/v_1(\text{RCl}_2)$ ratio is equal to 1.191 ± 0.008 . Within the error of determination, this value coincides with the analogous ratio $v_1(\text{RF}_3)/v_1(\text{RF}_2)$. Indeed, if the molecular constants of RF₃ from Kovács and Konings (2004), which were used for calculating the thermodynamic functions of these compounds, are corrected for the matrix shift of $+15 \text{ cm}^{-1}$, the $v_1(\text{RF}_3)/v_1(\text{RF}_2)$ ratio becomes equal to 1.179 ± 0.009 . This allows us to draw the conclusion that the v_1 frequency of lanthanide difluorides can be reliably calculated from the v_1 values for trifluorides with the use of the $v_1(\text{RF}_3)/v_1(\text{RF}_2)$ ratio.

Comparative analysis of the experimental data on RCl₂ (Chervonnyi and Chervonnaya, 2003) has also confirmed the constancy of the v_3/v_1 ratio in these compounds. This principle is basic in determining the v_3 values from the v_1 values. After correcting the v_3 values for the matrix shift (+15 cm⁻¹), the $v_3(RF_2)/v_1(RF_2)$ ratio is equal 0.96 \pm 0.01. The use of this ratio and of v_1 values for RF₂ make it possible to determine the v_3 values for all difluorides. It is worth noting that the deviations of the calculated v_3 frequencies from the experimental data (DeKock et al., 1972; Hastie et al., 1971) are only 0.8 (SmF₂), 4.6 (EuF₂), and 5.6 (YbF₂) cm⁻¹.

The bending vibration frequency of EuF_2 measured by Hastie et al. (1971) in two matrices is virtually the same, and the use of a mean value is recommended.

Comparison of the experimental and theoretical data of Kovács and Konings (2004) with the molecular constants for RF₃ shows that the bending vibrational frequencies were not corrected for matrix shift. In the calculation of the molecular constants of RCl₂, we also did not correct the v_2 frequencies for matrix shift (Chervonnyi and Chervonnaya, 2004g); rather, we accepted that the v_3/v_2 and v_1/v_2 ratios are constant for dichlorides and are equal to the same ratios as found for EuCl₂. The calculation of

 v_2 for lanthanide difluorides was performed analogously and based on the available value for EuF₂.

The R_e value accepted for EuF₂ by Hastie et al. (1971) has been estimated based on the data from Vilkov et al. (1967) for structurally similar compounds and is presumably overestimated. This conclusion follows from a comparison of the interatomic distances in the series RCl₃–RCl₂–RCl (see Chervonnyi and Chervonnaya, 2003, 2004d,g) and RF₃–RF₂–RF. For fluorides, the interatomic distances for RF₃ were estimated from the of Kovács and Konings (2004) and the one for RF from the data of Chervonnyi and Chervonnaya (2004d). This comparison shows that the estimate according to which the bond lengths in the trifluorides are 0.062 Å shorter than in the corresponding difluorides is more reliable. Inasmuch as $R_e(R-F)$ in RF₃ was taken to be a linear function of lanthanide atomic number (Kovács and Konings, 2004), the estimation method used implies that the same linearity is transferred to the dependence of $R_e(R-F)$ for RF₂ molecules, although the effect of lanthanide contraction on the molecular constant under consideration is thereby ignored.

The $\angle_{e}(F-Eu-F)$ angle value suggested by Hastie et al. (1971) was determined from the intensity ratio of bands observed in IR spectra and was confirmed by valence force field calculations of the force constants of EuF₂, as well as of its possible structural analogues, CaF₂ and SrF₂. After similar spectral analysis and valence force field calculations (although with different force constants), the bond angles in SmF₂ and YbF₂ were reported by DeKock et al. (1972) to be 110° (the same as in EuF₂) and 140°, respectively.

However, spectral and electron diffraction data for RCl₂ (Chervonnyi and Chervonnaya, 2003) show that such a considerable difference in bond angle between SmF₂ and EuF₂, on one hand, and YbF₂, on the other hand, is unrealistic. The range of bond angles is, as a rule, considerably narrower in going from lanthanum to lutetium compounds. The bond angle values used in calculating the thermodynamic functions for RF₃ (Chervonnyi and Chervonnaya, 2007a), RCl₃ (Chervonnyi and Chervonnaya, 2004g), and RCl₂ (Chervonnyi and Chervonnaya, 2003) are within the range 109.0–116.0°, 115.4–117.9°, and 132.9–141.3°, respectively. Based on the bond angles obtained for these compounds, the bond angles for the compounds under consideration were estimated by interpolation taking into account the data of Hastie et al. (1971) and DeKock et al. (1972). The dependence of the $\angle_{e}(F-R-F)$ values thus obtained on *n*, which is linear like that of $R_{e}(R-F)$, is presented in Table 8, along with other relations of type (1) used for calculating the molecular constants of RF₂. According to our estimates, the $\angle_{e}(F-R-F)$ values for SmF₂ (118.5°) and EuF₂ (120.0°) are higher and that for YbF₂ (130.5°) is lower than the corresponding angles reported by Hastie et al. (1971) and DeKock et al. (1972).

P _i (n)	A _i	B _i	C _i
$v_1 (cm^{-1})$	439.39015	6.11100	-0.17163
$v_2 ({\rm cm}^{-1})$	105.73014	1.47049	-0.04130
$v_3 ({\rm cm}^{-1})$	421.58599	5.86341	-0.16468
R(R-F) (Å)	2.14891	-0.00959	0
\angle (F—R—F) (°)	109.5	1.5	0

TABLE 8 Molecular constants of RF₂

The proposed $\angle_{e}(F-R-F)$ values for SmF₂, EuF₂, and YbF₂ are larger than the $\angle_{e}(F-Ba-F)$ angle used by Gurvich et al. (1978–1984) in the calculation of the thermodynamic functions for BaF₂ ($\angle_{e}(F-Ba-F) = 100 \pm 10^{\circ}$). Such a difference is qualitatively confirmed by electric deflection studies (Kaiser et al., 1972) on molecular beams of the four compounds.

Comparison of our data and those of Jia (1990) shows that only bond lengths are in satisfactory agreement, the differences in these parameters being within ± 0.04 Å. We note that the estimates of Jia (1990) were made using an empirical relationship that relates the ionic radii (Shannon, 1976) in crystals to the interatomic distances in gaseous RF₂ molecules. The difference in the other molecular constants is considerably larger. In particular, the use of Ohwada's model (1980) for lanthanide difluorides leads to the underestimation of stretching vibrational frequencies and to the overestimation of the bending vibrational frequency. The same phenomenon has been observed for NdI₂ and SmI₂ (Ezhov and Sevast'yanov, 2001, 2004).

A few years ago, the molecular constants of dysprosium halides were calculated by the quantum-chemical DFT/B3LYP method (Saloni et al., 2004). The data obtained for dysprosium difluoride and dichloride are compared in Table 9 with analogous values recommended by us. As follows from Table 9, the results are in good agreement, except for the vibrational frequencies v_2 and v_3 of DyF₂. Their clearly overestimated values and, which is especially important, the fact that $v_3 > v_1$, cast doubt on the reliability of these values. The ratio between the stretching vibrational frequencies in lanthanide halides was already mentioned by us (Chervonnyi and Chervonnaya, 2004g) when examining available experimental data on trihalides. This is also confirmed by the results of *ab initio* calculations of the molecular constants of ErF₂ and TmF₂ (Lesar et al., 1998), which are in satisfactory agreement with our estimates (Table 9).

3.2.2 Electronic states

Our approach to the calculation of this contribution to the thermodynamic functions has been explained in detail for RCl_3 , RF_3 (see Section 2), and RCl_2 . The inclusion of the electronic state energies (<10,000 cm⁻¹) of the of R^{3+} and R^{2+} ions with the use of data from

	R(R—X)	∠(X—R—X)	v ₁	v ₂	v ₃	
RX ₂	(Å)	(°)	(cm ⁻¹)	(cm ⁻¹)		
DyCl ₂	2.531	138.3	276.9	65.3	289.7	а
<i>y</i> –	2.549	131.3	274.3	69.7	287.8	b
DyF ₂	2.053	124.5	483.4	116.3	463.8	С
5 -	2.047	123.9	487.2	147.4	504.1	b
ErF ₂	2.034	127.5	487.9	117.4	468.2	С
-	2.046	122	540	112	525	d
TmF ₂	2.024	129.0	489.9	117.9	470.0	С
-	2.036	123.1	543	112	530	d

 TABLE 9
 Comparison of the molecular constants of some RX2

^a Chervonnyi and Chervonnaya (2004c).

^b Saloni et al. (2004).

^c Chervonnyi and Chervonnaya (2007c).

^d Lesar et al. (1998).

Martin et al. (1978) commonly involves taking into account the Stark splitting of the ground-state term of the ions. For R^{3+} ions, the splitting values were taken from Morrison and Leavitt (1982) and from original works (Carnall et al., 1976, 1977). The lack of corresponding data for R^{2+} ions forced us to study the correlations between the energy levels of similar terms of R_n^{2+} ions and isoelectronic R_{n+1}^{3+} ions (here, n = 1-15 is the atomic number of a 4f element in the lanthanide series) and to suggest the polynomial equation (2) which makes possible the calculation of excitation energies for the R^{2+} electronic states.

The Stark splitting of the ground states of Ce^{2+} , Pr^{2+} , Nd^{2+} , Pm^{2+} , Tb^{2+} , Dy^{2+} , Ho^{2+} , Er^{2+} , and Tm^{2+} was estimated with the use of polynomial (2) and the splittings of the ground-state multiplets of R^{3+} ions in a fluoride ligand field reported by Chervonnyi and Chervonnaya (2007a). For Pm^{2+} and Dy^{2+} , the energies of all states under consideration were calculated by polynomial (2). This procedure was not used for estimating the splitting of the ground state in La^{2+} and Gd^{2+} ions since their ground-state configurations differ from those of the isoelectronic ions Ce^{3+} and Tb^{3+} . In addition, Stark splitting does not exist for Sm^{2+} , Eu^{2+} , Yb^{2+} , and Lu^{2+} ions. The energies of electronic states and their statistical weights in gaseous RF_2 molecules that were used in calculations of the thermodynamic functions are presented in Table 10.

3.2.3 Thermodynamic functions

Thermodynamic functions were calculated in the rigid rotator–harmonic oscillator approximation for the ideal gas state at the standard pressure and in the temperature range 298.15–3000 K. These functions are given in Table A4 in the form of the f_i coefficients (see Appendix).

R	Ground state	Electronic state energies (cm ⁻¹) and their statistical weights (within parentheses)
La	${}^{2}D_{3/2}$	0(4), 1603.23(6), 7195.14(6), 8695.41(8)
Ce	⁻ Π ₄	0(1), 43(1), 50(1), 98(1), 147(1), 161(1), 210(1), 240(1), 362(1), 1528.32(11), 3127.10(13), 3276.66(9), 3762.75(5), 3821.53(5), 4764.76(7), 5006.06(9), 5127.27(9), 5502.37 (7), 6265.21(7), 6361.27(11), 6571.36(5), 7150.05(9), 7120.00(9), 7836.72(9), 8349.99(13), 8922.05(2), 9325.51(11), 9900.49(5)
Pr	⁴ I _{9/2}	0(2), 33(2), 101(2), 220(2), 372(2), 1398.34(12), 2893.14(14), 4453.76(16), 9370.66(4)
Nd	${}^{5}I_{4}$	0(2), 69(2), 88(1), 105(2), 133(1), 252(1), 1137.8(11), 2387.6(13), 3714.9(15), 5093.3(17)
Pm	⁶ H _{5/2}	0(2), 35(2), 124(2), 783(2), 817(2), 859(2), 926(2), 1786(10), 2816(12), 3893(14), 4907(2), 5047(16), 5102(4), 5500(6), 6171(8), 7083(10)
Sm	⁷ F ₀	0(1), 293.45(3), 813.55(5), 1492.66(7), 2277.88(9), 3131.54(11), 4026.99(13)
Eu	$8S_{7/2}$	0(8)
Gd	⁹ D ₂	0(5), 279.32(7), 694.37(9), 1310.13(11), 2282.83(13), 2381.24(13), 3996.71(11), 5015.20(9), 5789.97(7), 6334.17(5), 9195.04(9), 9356.30(11), 9717.70(9)
Tb	⁶ H _{15/2}	0(2), 35(2), 52(2), 93(2), 130(2), 176(2), 228(2), 392(2), 2804.67(14), 4734.52(12), 6258.08(10), 6470.11(12), 7422.21(8), 7621.556(10), 8285.885(6), 8972.29(14), 9144.98(8), 9218.63(12), 9275.42(16)
Dy	⁵ I ₈	0(2), 6.2(2), 16(1), 28(2), 46(1), 65(2), 88(1), 106(1), 126(2), 173(1), 179(2), 4272(15), 7233(13)
Но	${}^{4}I_{15/2}$	0(2), 44(2), 55(2), 82(2), 97(2), 98(2), 155(2), 196(2), 5438.53(14), 8644.59(12)
Er	³ H ₆	0(1), 58(1), 101(1), 134(1), 175(1), 202(1), 234(1), 235(1), 300 (1), 304(1), 344(1), 356(1), 379(1), 5081.79(9), 6969.78(11)
Tm	$^{2}F_{7/2}$	0(2), 67(2), 159(2), 346(2), 8774.02(6)
Yb	${}^{1}S_{0}$	0(1)
Lu	$^{2}S_{1/2}$	0(2), 5707.6(4), 8647.8(6)

TABLE 10 Electronic states of R^{2+} in $RF_2(g)$

The thermodynamic functions of LaF_2 determined by other authors differ noticeably from our data. For example, the reduced Gibbs energy at 2000 K we found is ~12 and 22 J/(mol·K) higher than the corresponding energies published by Hildenbrand and Lau (1995) and Krasnov and Danilova (1969), respectively. These significant discrepancies are caused, first, by noticeable differences in the molecular constants used and, second, by the noninclusion of excited electronic states, as well as by the fact that the statistical weight of the ground state was taken to be 2.

Considering possible errors in the estimation of the molecular constants (± 0.01 Å for bond lengths, ± 5 cm⁻¹ for vibration frequencies, and $\pm 2^{\circ}$ for bond angles), as well as the additional error introduced into the reduced Gibbs energy by the uncertainty in electronic excitation energies, the overall error for $- [G^{\circ}(T) - H^{\circ}(0)]/T$ (RCl₂(g) and RF₂(g)) is no more than ± 3 J/(mol·K).

4. THERMODYNAMIC PROPERTIES OF LANTHANIDE TRIFLUORIDES

Although thermochemical properties of lanthanide di- and trichlorides have long been studied, available data are insufficient for reliable thermodynamic modeling of high-temperature processes implying these compounds. In particular, there is no complete set of thermodynamic functions including heat capacity $C_p^{\circ}(T)$, entropy $S^{\circ}(T)$, enthalpy $H^{\circ}(T) - H^{\circ}(298)$, and reduced Gibbs energy $- [G^{\circ}(T) - H^{\circ}(298)]/T$, for RCl_k (R = La–Lu, and k = 2, 3). The last compilation (Barin, 1995) contains thermodynamic functions for virtually all trichlorides (except PmCl₃ and LuCl₃) but only for one dichloride (YbCl₂) calculated from experimental data obtained before 1990.

Since then, however, additional studies of some thermodynamic parameters used in the calculations of $H^{\circ}(T) - H^{\circ}(298)$ and $-[G^{\circ}(T) - H^{\circ}(298)]/T$ have appeared. In particular, new results for RCl₃ (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, and Tm) and EuCl₂ were obtained (Da Silva et al., 2001; Gaune-Escard et al., 1994, 1996; Rycerz and Gaune-Escard, 2002a,b,c). A comparison of the data contained in Barin (1995) and those reported by Gaune-Escard et al. (1994, 1996), Da Silva et al. (2001), and Rycerz and Gaune-Escard (2002a,b,c) reveals obvious differences in high-temperature heat capacities (T > 350 K). Additional phase transitions have also been observed in the solid state and the thermodynamic functions for SmCl₃, EuCl₃, and TmCl₃ calculated by Rycerz and Gaune-Escard (2002b,c) substantially deviate from those presented by Barin (1995).

The thermodynamic functions reported in (Barin, 1995) for RCl₃ (R = La–Gd) were calculated using heat capacities (Sommers and Westrum, 1976, 1977) reliably measured in the low-temperature range (<350 K). For the other trichlorides, estimates from the early 1980s have been used. As a result, experimental data on heat capacities of RCl₃ (R = Dy, Ho, Er, Tm, Yb, and Lu) over the temperature range \sim 6–340 K (Gorbunov et al., 1986; Tolmach et al., 1987c, 1988, 1990b,c,d) remained unexploited. Likewise,

similar heat capacity measurements (Gavrichev et al., 1987a,b; Tolmach et al., 1986, 1987a,b, 1988) performed for several RCl_2 (R = Nd, Sm, Eu, Dy, Tm, and Yb) compounds have not been taken into consideration.

Our processing of experimental data on lanthanum, samarium, europium, and ytterbium chlorides (Chervonnyi and Chervonnaya, 2004a,b,e, f_{t} 2005b) shows that the available thermodynamic functions for condensed state cannot be used to bring in coincidence the calculated enthalpies of atomization $\Delta_{at}H^{\circ}(298)$ of a given chloride with those determined by measuring its saturated vapor pressure, equilibrium constants of gas-phase reactions in the R + BaCl₂ systems, and fragment ion appearance energies. In these calculations, reliable enthalpies of formation of crystalline compounds $\Delta_{f}H^{\circ}(cr, 298)$ (Chervonnyi and Chervonnaya, 2005c; Cordfunke and Konings, 2001a) and thermodynamic functions (Chervonnyi and Chervonnaya, 2003, 2004g) of gaseous chlorides were used. We therefore revised the thermodynamic functions of the condensed state (Chervonnyi and Chervonnaya, 2004a,b,e,f, 2005b). This work led us to conclude that the description of these functions based on a nonsystematic analysis encounters difficulties. The spread of separate thermophysical characteristic values is too large. In our view, errors in these values are determined by two factors. These are the purity of the initial substances and care in the preparation and conduction of measurements. The last factor owes its importance to the very high hygroscopicity of lanthanide chlorides. Their interaction with moisture at any stage of measurements can substantially distort the final results.

4.1 Method for calculating thermodynamic functions

To reliably select separate thermodynamic parameters for the compounds under consideration, we must improve the suitable calculation procedures and/or criteria that allow the validity of the available experimental data to be estimated. To this end, we have selected lanthanide trifluorides as example. They are much less sensitive to hydrolysis although they have noticeable corroding action on container materials at high temperatures. In view of this, we have chosen the method of heat capacity calculations over a wide temperature range, up to the melting point, based on an analysis of the experimental low-temperature heat capacities and high-temperature enthalpy increments. This method is described below. Its application to lanthanide di- and trichlorides will be presented later on.

Note that the description of the thermodynamic functions for all lanthanide trifluorides undertaken in this work is of importance because the corresponding data were reported by Barin (1995) for R = La, Ce, Pr, Nd, Eu, Gd, Dy, and Ho only.

4.1.1 Calculation of heat capacity of crystalline compounds

The thermodynamic functions of the condensed state are calculated mainly based on the preliminary description of the temperature dependence of heat capacity $C_p^{\circ}(T)$ in the temperature interval of interest taking into account phase transitions within this interval. In order to reveal trends in $C_p^{\circ}(T)$ changes over series of similar lanthanide compounds, we have analyzed the adiabatic calorimetry data obtained at ~5–350 K for sulfides R₂S₃ (Demlow et al., 1998; Gruber et al., 1991, 1993, 1999, 2000; Shaviv et al., 1992; Westrum et al., 1989), oxides R₂O₃ (Gruber et al., 1982, 2002; Justice and Westrum, 1963a,b,c, 1969; Justice et al., 1969), hexaborides RB₆ (Novikov, 2001, 2003; Sirota et al., 2002; Westrum et al., 2002, b), hydroxides R(OH)₃ (Chirico et al., 1979, 1981; Chirico and Westrum, 1980a,b, 1981), anhydrous trichlorides RCl₃ (Sommers and Westrum, 1976, 1977) and their crystal hydrates RCl₃·6H₂O (Spedding et al., 1972), and trifluorides RF₃ (Flotow and O'Hare, 1981, 1984; Lyon et al., 1978, 1979a,b; Westrum and Beale, 1961).

Although these studies were largely directed toward the determination of the heat capacity $C_p^{\circ}(298)$ and entropy $S^{\circ}(298)$ values at standard temperature (298.15 K), they were also concerned with an important problem of proving the existence of contributions to the heat capacity (accordingly, entropy) of lanthanide compounds caused by the excitation of electronic states. In particular, because the upper boundary of the temperature interval was fairly low, splitting of the ground electronic states of molecules under the action of ligand crystal field was studied. That is, the existence of the so-called Schottky contribution to or Schottky anomaly in thermophysical values was elucidated.

The techniques used in data processing and trends revealed thereby are of key importance for determining approaches to solving the problem of analytically describing the temperature dependence of heat capacity over a fairly broad temperature interval. We therefore describe the essence of these studies.

Westrum (1979) assumed that the heat capacity of a pure crystalline substance at a constant pressure could be represented by the sum of its separate components as

$$C_{\rm p}^{\circ} = C_{\rm v}^{\circ} + C_{\rm e}^{\circ} + C_{\rm m}^{\circ} + C_{\rm Sch}^{\circ} + C_{\rm d}^{\circ},$$
 (3)

where C_v is the lattice (vibrational) component of the heat capacity at a constant volume, C_e is the contribution from electronic conductivity, C_m is the contribution related to cooperative magnetic ordering, C_{Sch} is the contribution of noncooperative magnetic ordering (Schottky's contribution), and C_d is the contribution to the heat capacity related to crystal thermal expansion.

In fact, the contribution of electronic conductivity can be ignored because it is quite small. The major contribution to C_p° arises from the lattice (vibrational) component C_v° , which varies linearly as a function of molar volume *V* in a series of isomorphous compounds. For the compounds under study, C_v° can therefore be estimated using volume-weighted interpolation (Westrum et al., 1989) and data on isomorphous diamagnetic substances as reference values. For instance, the C_v° heat capacities measured for trivalent lanthanum, gadolinium, and lutetium compounds were used as reference values. Subsequently, the C_m° and C_{Sch}° contributions from the experimental C_p° values.

Justice and Westrum (1963a,b,c) studied the influence of the magnetic contribution and Schottky's anomaly on the heat capacities of lanthanide compounds. They proved that the C_{m}° and C_{Sch}° contributions determined from heat capacity measurements were in agreement with the results of their calculations. A similar problem was solved in studying the behavior of lanthanide compounds in magnetic fields at superlow temperatures, for the example in the case of RCl₃ (Colwell et al., 1969; Eisenstein et al., 1965; Krämer et al., 1999; Landau et al., 1973; Zassenhaus et al., 1998). For this purpose, the agreement between the experimental and calculated magnetic entropy $S_{\rm m}^{\circ}$ component has been first checked. For instance, this contribution amounts to $S_m^{\circ} = R\ln(8)$ for trivalent gadolinium compounds and to $S_{\rm m}^{\circ} = R \ln(2)$ for the other lanthanide compounds with a statistical weight for the ground state equal to 2. It has been found that, as a rule, the experimental $S_{\rm m}$ value was about 0.8–0.85 that of the theoretical value. Second, the excess contribution to heat capacity of the Schottky's anomaly have been determined and compared with the value calculated from spectroscopic data or data from the theoretical determination of ground electronic state splitting. The degree of correspondence between them has been assessed. In the majority of cases, agreement between these values was satisfactory. Note that the spectral data obtained for pure compounds have been used for this purpose. Theoretical calculations of the splitting of the ground electronic state have been further performed taking into account the influence of different anion on the lanthanide cations according to their anion localization in the lattice.

The trends initially established for the temperature dependence of C_p° over a narrow temperature interval have also been studied at high temperatures. In particular, very important results have been obtained by Gruber et al. (2002) who have established the correctness of the approach to the description of heat capacity. The authors showed for example that the experimental data on La₂O₃ and Nd₂O₃ can be used to obtain C_p° for intermediate compounds (Ce₂O₃ and Pr₂O₃) in close agreement with high-temperature heat capacity measurements (up to 1000 K). Importantly, the lattice components have been estimated for Ce₂O₃ and

Pr₂O₃ using the lattice component for Nd₂O₃ as a reference value after subtracting additional contributions from its heat capacity.

In this work, we make an attempt to describe the experimental $C_p^{(T)}(T)$ values for RF₃ (Flotow and O'Hare, 1981, 1984; Lyon et al., 1978, 1979a,b; Westrum and Beale, 1961) in an analytic form. Our aim is to reveal trends in variation of parameters. Our description is based on the additive dependence of $C_p^{(T)}(T)$ on the separate components of Eq. (3).

The lattice component was calculated using the harmonic approximation, in which all the acoustic and low-frequency optical vibrations are included with the help of a single Debye function, while high-frequency crystal vibrations are taken into account by Einstein's equation. According to Kelley's derivations (Gurvich et al., 1978–1984) based on the Born-von Karman dynamic crystal lattice theory, we therefore have

$$C_{\rm v}^{\rm o}(T) = 3R \left[D\left(\frac{\theta_{\rm D}}{T}\right) + \sum_{i=1}^{n-1} E\left(\frac{\theta_{\rm Ei}}{T}\right) \right],\tag{4}$$

in which *n* is the number of atoms in the molecule, $D(\theta_D/T)$ is the Debye function with the characteristic Debye temperature θ_D , and $E(\theta_{Ei}/T)$ is the Einstein function with the characteristic Einstein temperature θ_{Ei} .

The thermal expansion of crystals, that is, the transition to the quasiharmonic approximation in calculations of the temperature dependence of heat capacity (Demlow et al., 1998), was included using Lord–Ahlberg– Andrews' equation (Lord et al., 1937)

$$C_{\rm d}^{\circ}(T) = \alpha T \left[C_{\rm v}^{\circ}(T) \right]^2 \tag{5}$$

where α is a constant characterizing the substance.

The $C_{lat}^{\circ}(T)$ function describing the sum of the $C_{v}^{\circ}(T)$ and $C_{d}^{\circ}(T)$ contributions therefore takes the form

$$C_{\text{lat}}^{\text{o}}(T) = 3R \left[D\left(\frac{\theta_{\text{D}}}{T}\right) + \sum_{i=1}^{n-1} E\left(\frac{\theta_{\text{Ei}}}{T}\right) \right] + 9R^{2}\alpha T \left[D\left(\frac{\theta_{\text{D}}}{T}\right) + \sum_{i=1}^{n-1} E\left(\frac{\theta_{\text{Ei}}}{T}\right) \right]^{2}.$$
 (6)

Calculations of the excess contribution $C_{exs}^{\circ}(T)$ for taking into account the excitation of electronic states were performed according to the classical theory.

Using the partition function Q(T) for a system of *n* energy levels with energies ε_i and degeneracy g_i ,

$$Q(T) = \sum_{i=0}^{n} g_i \exp\left(-\frac{\varepsilon_i}{RT}\right),$$

we can write heat capacity as a function of temperature in the form

$$C_{\text{exs}}^{\circ}(T) = R^{-1}T^{-2} \Big[E_1(T) - (E_2(T))^2 \Big],$$
 (7)

where

$$E_1(T) = \frac{\sum_{i=0}^n g_i \varepsilon_i^2 \exp(-\varepsilon_i / RT)}{Q(T)}$$

and

$$E_2(T) = \frac{\sum_{i=0}^{n} g_i \varepsilon_i \exp(-\varepsilon_i / RT)}{Q(T)}$$

Calculations were performed as follows. Where necessary, the $C_{exs}^{\circ}(T)$ contribution calculated by Eq. (7) was subtracted from the experimental low-temperature heat capacities of LaF₃ (Lyon et al., 1978), CeF₃ (Westrum and Beale, 1961), PrF₃ (Lyon et al., 1979a), NdF₃ (Lyon et al., 1979b), GdF₃ (Flotow and O'Hare, 1981), DyF₃ (Flotow and O'Hare, 1984), ErF₃ (Flotow and O'Hare, 1984), and LuF₃ (Flotow and O'Hare, 1981). For each compound, these data included, as a rule, from 60 to 90 $C_p^{\circ}(T)$ values measured over the temperature range ~4.6–348 K. The sequence of the $C_{lat}^{\circ}(T)$ values formed this way was approximated by the method of least squares according to Eq. (6). This approximation was used to calculate the variable parameter θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α . The Debye function in Eq. (6) was found using the converging series (Losch, 1961)

$$D\left(\frac{\theta_{\rm D}}{T}\right) = \frac{4}{5}\frac{\pi^4}{x^3} - \sum_{n=1}^{\infty} \left[3(nx) + 12 + \frac{36}{nx} + \frac{72}{(nx)^2} + \frac{72}{(nx)^3}\right] \frac{{\rm e}^{-nx}}{n},$$

where $x = \theta_{\rm D}/T$.

In Debye function calculations, the series was truncated after achieving the required accuracy. As a rule, no less than 50 series members were included.

In certain instances, the characteristic Debye temperature was determined from partial data obtained at the lowest measurement temperatures prior to the approximation of the complete set of experimental data according to Eq. (6). The approximating function then had the form

$$C_{\rm p}^{\circ}(T) = 3RD\left(\frac{\theta_{\rm D}}{T}\right) + 9R^2\alpha T \left[D\left(\frac{\theta_{\rm D}}{T}\right)\right]^2 + C_{\rm exs}^{\circ}(T)$$
(8)

The inclusion of the $C_{exs}^{\circ}(T)$ contribution into Eq. (8) means that the splitting energies of the ground term were variable parameters for compounds for which this contribution was nonzero. If $\theta_{\rm D}$ was calculated by

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Eq. (8), this parameter was not varied in approximating the experimental data by Eq. (6) over the complete range of measurements.

In some instances, it was useful to approximate the difference between the experimental heat capacity values and the heat capacities calculated by Eq. (6) using the known characteristic parameter values. Such an approximation with the use of Eq. (7) allowed us to put the variable energies of separate levels in correspondence with the accepted tabulated values.

4.1.2 Calculations of $C_{p}^{\circ}(298)$ and $S^{\circ}(298)$

All excess contribution $C_{exs}^{\circ}(T)$ calculations were performed using the splitting energies of the ground term listed in Table 5. The energies of the other excited electronic states were set equal to the electronic state energies of \mathbb{R}^{3+} ions, according to Martin et al. (1978).

The variable approximation parameter values (θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α) as functions of the molar volumes V_{RF_3} calculated from the X-ray data (ICDD Database, 1993) form fairly accurate linear dependences (see Figure 7) for two series of RF₃ (R = La–Pm, and R = Sm–Lu). The separation into two series is caused by the formation of different polymorphs by these compounds. Under standard conditions, lanthanide trifluorides from lanthanum to promethium inclusive have LaF₃-type structures, in which the CN of R is 6. All the other RF₃ are characterized β -YF₃-type crystal structures with the CN = 9.

The coefficients of the equations describing these parameters in the RF_3 series were calculated by the least-squares method. These data on RF_3 (R = Sm—Lu) were obtained without taking into account the results



FIGURE 7 Dependence of the θ_D values (*left*), and the α values (*right*) on molar volume in the series of RF₃ compounds.

found in processing experimental data (Flotow and O'Hare, 1984) on the heat capacity of ErF₃. For this compound, we were unable to obtain the θ_{D} , θ_{E1} , θ_{E2} , θ_{E3} , and α parameters in agreement with similar data for the other RF₃. We found that the subtraction of $C_{exs}^{\circ}(T)$ from $C_{p}^{\circ}(T)$ reported by Flotow and O'Hare (1984) gave negative $C_{lat}^{\circ}(T)$ values at low temperatures.

After the analytic equations for calculating θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α were established, we calculated numerical values for these parameters (see Table 11) and solved the inverse problem of the determination of the heat capacity for each of the lanthanide trifluorides (Eq. (9)), both at an arbitrary temperature of interest and over the necessary temperature range,

$$C_{\rm p,cal}^{\circ}(T) = C_{\rm lat}^{\circ}(T) + C_{\rm exs}^{\circ}(T).$$
(9)

The $C_{lat}^{\circ}(T)$ and $C_{exs}^{\circ}(T)$ values were calculated by Eqs. (6) and (7). Calculations of $C_{p}^{\circ}(T)$ were performed with the discrete temperature intervals compatible for subsequent numerical integration to determine $S^{\circ}(T)$.

The heat capacities and entropies under standard conditions obtained in our calculations and reported experimentally by several autors (Flotow and O'Hare, 1981, 1984; Lyon et al., 1978, 1979a,b; Westrum and Beale,

	V _{RF3}					$\alpha imes 10^7$
R	(cm³∕mol)	Θ_{D} (K)	Θ_{E1} (cm ⁻¹)	Θ_{E2} (cm ⁻¹)	Θ_{E3} (cm ⁻¹)	(mol⁄J)
La	33.00	178.76328	200.87393	262.61921	391.60785	9.52997
Ce	32.19	182.21327	203.07650	267.14004	397.83545	9.55217
Pr	31.49	185.19475	204.97995	271.04693	403.21732	9.57135
Nd	30.92	187.62253	206.52991	274.22825	407.59970	9.58697
Pm	30.36	190.00772	208.05267	277.35376	411.90520	9.60232
Sm	31.23	195.29901	213.47886	285.69968	412.15827	9.59918
Eu	30.68	197.67461	215.08880	290.11417	417.36646	9.61373
Gd	30.35	199.09997	216.05476	292.76287	420.49138	9.62245
Tb	29.85	201.25960	217.51834	296.77604	425.22611	9.63568
Dy	29.42	203.11689	218.77702	300.22737	429.29797	9.64705
Но	29.00	204.93098	220.00643	303.59844	433.27514	9.65816
Er	28.66	206.39953	221.00166	306.32740	436.49475	9.66715
Tm	28.39	207.56573	221.79200	308.49451	439.05150	9.67430
Yb	28.14	208.64555	222.52379	310.50110	441.41887	9.68091
Lu	27.97	209.37983	223.02140	311.86558	443.02867	9.68540
Tm Yb Lu	28.39 28.14 27.97	207.56573 208.64555 209.37983	221.79200 222.52379 223.02140	308.49451310.50110311.86558	439.05150 441.41887 443.02867	9.67430 9.68091 9.68540

TABLE 11 Molar volumes and characteristic parameters for calculating the latticecontribution to the heat capacity of lanthanide trifluorides a

^a The listed values are vibrational frequencies rather than Einstein's characteristic temperatures; these frequencies can conveniently be compared with those of IR and Raman bands. Transformation of frequencies into characteristic temperatures is performed by multiplying frequencies by 1.43879 K·cm.

	C _p (298)	S°(298)	C _P (298)	S°(298)
R	Experimental		Calculated	
La	90.29 ± 0.09^{a}	106.98 ± 0.11^{a}	90.32	107.09
Ce	93.47 ^b	115.23 ^b	92.15	119.42
Pr	92.65 ± 0.09^{c}	121.22 ± 0.12^{c}	92.20	121.23
Nd	92.42 ± 0.09^d	120.79 ± 0.12^{d}	92.16	120.82
Pm	-	-	90.78	120.26
Sm	_	_	91.54	115.73
Eu	_	-	98.23	109.27
Gd	88.39 ± 0.09^{e}	114.77 ± 0.22^{e}	88.41	116.35
Tb	_	-	90.38	118.25
Dy	89.94 ± 0.09^{f}	118.07 ± 0.12^{f}	89.76	119.22
Ho	_	-	88.50	119.74
Er	90.07 ± 0.09^{f}	116.86 ± 0.12^{f}	88.30	118.62
Tm	_	-	90.67	115.09
Yb	_	-	89.42	110.92
Lu	87.07 ± 0.09^{e}	94.83 ± 0.09^{e}	87.09	94.82

TABLE 12 $C_{p}(298)$, and $S^{\circ}(298)$ values (in J/(mol·K)) for RF₃

^{*a*} Lyon et al. (1978).

^b Westrum and Beale (1961).

^c Lyon et al. (1979a).

^d Lyon et al. (1979b).

^e Flotow and O'Hare (1981).

^f Flotow and O'Hare (1984).

1961) are summarized in Table 12. Scrutiny of these values shows that, on the whole, the scheme suggested by us for the calculations of $C_p^{\circ}(T)$ leads to a good agreement for both $C_p^{\circ}(298)$ and $S^{\circ}(298)$. In several instances, the differences between the two sets of data were as small as some hundredths of J/(mol·K).

Note that substantial deviations of the calculated parameters from the literature data appear in three instances. First, a discrepancy between S° (298) values is observed for GdF₃ in spite of close $C_{p}^{\circ}(298)$ values. This is related to the procedure used for including the S_{m}° contribution. We calculated this contribution according to the theoretical equation considering the statistical weight of the ground state. Next, not coinciding values were, as expected, obtained for ErF₃. In our view, this was caused by errors in both the experimental data and energy levels for the ground electronic state. Lastly, the most surprising discrepancy was that between the experimental data (Westrum and Beale, 1961) and calculated values for CeF₃. We find difficulty in explaining this result because all the data reported by Westrum et al. are characterized by very high reliability. The contribution of Westrum's team to both theory and experiment is of great

importance for the development of modern concepts of the influence of Schottky's anomaly on the thermophysical properties of substances. The scope of these studies is much broader than what is mentioned in the present work.

4.1.3 Dependence of $C_{p}^{\circ}(T)$ at 298 < T < T_{m}

The applicability of the suggested procedure to the description of heat capacity at high temperatures, up to the melting point T_m , was estimated by comparing $C_{p, cal}^{\circ}(T)$ and $C_{p, exp}^{\circ}(T)$ values. The latter were calculated from the calorimetric data on enthalpy increments obtained for LaF₃ (Lyon et al., 1978; Spedding and Henderson, 1971), CeF₃ (Charlu et al., 1970; Spedding et al., 1974), PrF₃ (Charlu et al., 1970; Spedding and Henderson, 1971), SmF₃ (Spedding et al., 1974), EuF₃ (Spedding et al., 1974), GdF₃ (Charlu et al., 1970; Spedding et al., 1974), EuF₃ (Spedding et al., 1974), GdF₃ (Charlu et al., 1970; Spedding et al., 1974), EuF₃ (Spedding et al., 1974), ThF₃ (Spedding et al., 1970; Lyapunov et al., 2000b; Spedding et al., 1974), HoF₃ (Lyapunov et al., 2000a; Spedding et al., 1974), YbF₃ (Charlu et al., 1974), TmF₃ (Spedding et al., 1974), YbF₃ (Charlu et al., 1974), and LuF₃ (Lyapunov et al., 2004; Spedding et al., 1974).

The list of compounds studied in Lyon et al. (1978), Charlu et al. (1970), Spedding and Henderson (1971), Spedding et al. (1974), Lyapunov et al. (2000a,b, 2004) includes all RF₃ (except PmF₃). For several compounds, such studies were performed twice and even three times for GdF₃ and DyF₃. A joint analysis of the $C_{p, exp}^{\circ}(T)$ values from these works (the hightemperature heat capacity data) and the results reported in Westrum and Beale (1961), Lyon et al. (1978, 1979a,b), Flotow and O'Hare (1981, 1984) (the low-temperature data) reveals at least three special features of the results reported in Lyon et al. (1978), Charlu et al. (1970), Spedding and Henderson (1971), Spedding et al. (1974), and Lyapunov et al. (2000a,b, 2004) which are of importance for our purposes (see Figures 8 and 9).

First, all measurements by Lyon et al. (1978), Charlu et al. (1970), Spedding and Henderson (1971), Spedding et al. (1974), and Lyapunov et al. (2000a,b) were performed in such a way that high-temperature heat capacity calculations on the basis of these results are only possible starting at ~400 K. Therefore, direct comparison cannot be made for the overlapping temperature intervals of the low- and high-temperature $C_{p, exp}(T)$ ranges obtained using different techniques.

Modern methods allow such measurements to be made. For example, we can mention the determination of the heat capacity of BaCl₂ performed at both low and high temperatures. Goodman and Westrum (1966) reported measurements in the low-temperature range and Gardner and Taylor (1969) at high temperatures in order to determine the heat capacity of the same barium dichloride sample in both intervals. In the transition



FIGURE 8 High-temperature heat capacity data for CeF₃: (1) and (2), calculations by Eqs. (9) and (11), respectively; Δ , determined from the data reported by Charlu et al. (1970); and \bullet data from Spedding et al. (1974).



FIGURE 9 High-temperature heat capacity data for NdF₃: (1) and (2), calculations by Eqs. (9) and (11), respectively; Δ , determined from the data reported by Charlu et al. (1970); •, data from Spedding and Henderson (1971); and \bigcirc , low-temperature heat capacity data from Lyon et al. (1979b).

temperature range, these authors were able not only to perform measurements by both methods over a \sim 130 K temperature interval but also to obtain virtually coinciding values.

Second, several $C_{p, exp}^{\circ}(T)$ dependences in Lyon et al. (1978), Charlu et al. (1970), Spedding and Henderson (1971), Spedding et al. (1974), and Lyapunov et al. (2000a,b) were decreasing in the temperature region adjacent to the lower boundary of measurements, which resulted in the appearance of a minimum in the corresponding curves.

Lastly, there are discrepancies between heat capacity values obtained in these studies for the same compound that are outside measurement errors.

Nevertheless, a consistent comparison of $C_{p,cal}^{\circ}(T)$ and $C_{p,exp}^{\circ}(T)$ for each of the lanthanide trifluorides shows these values to coincide satisfactorily for at least one series of measurements. Such an agreement holds for most RF₃ compounds. The only exception is SmF₃ (Spedding et al., 1974), for which deviations from $C_{p,cal}^{\circ}(T)$ were too large in some temperature intervals. Enthalpy increment measurements ensure a ~3% instrumental accuracy (Jacobson et al., 1999) in the determination of heat capacity, and in the majority of cases, the deviation of calculated from experimental values is within 3% over the temperature range 400–1200 K.

There are data for which this difference is much smaller. For example, we can mention measurements of the thermophysical characteristics of LuF_3 by Lyapunov et al. (2004) (see Figure 10). A comparison of



FIGURE 10 High-temperature heat capacity data for LuF₃: (1) and (2), calculations by Eqs. (9) and (11), respectively; (3) data reported by Lyapunov et al. (2004); (Δ) data reported by Spedding and Henderson (1971); and (\bigcirc) low-temperature heat capacity data from Flotow and O'Hare (1981).

experimental data with the results of our calculations shows that the relative difference between $C_{p,exp}^{\circ}(T)$ and $C_{p,cal}^{\circ}(T)$ values does not exceed 1% over the temperature interval 298.15–680 K, ~2% at T = 700-1230 K, and increases to ~6% only at T > 1457 K.

A comparative analysis reveals a feature common to all data. At $T > ~ 0.5T_{\rm m}$, the experimental heat capacities are, as a rule, larger than the calculated values. This is characteristic of LaF₃ (Lyon et al., 1978; Spedding and Henderson, 1971), CeF₃ (Charlu et al., 1970; Spedding et al., 1974), NdF₃ (Charlu et al., 1970), EuF₃ (Spedding et al., 1974), DyF₃ (Lyapunov et al., 2000b), HoF₃ (Lyapunov et al., 2000a), YbF₃ (Spedding et al., 1974), and LuF₃ (Lyapunov et al., 2004). For DyF₃ (Charlu et al., 1970; Spedding et al., 1974), the above inequality holds starting with temperatures somewhat lower than $0.5T_{\rm m}$.

Systematic underestimation of the high-temperature $C_{p, cal}(T)$ data is a shortcoming of the quasi-harmonic approximation used to describe $C_{lat}(T)$. Westrum (1979) analyzed methods for including the contribution of crystal thermal expansion. It follows from the representation of $C_{d}(T)$ in the form of the dependence

$$C_{\rm d}^{\circ}(T) = \frac{\gamma^2 V T}{\beta} \tag{10}$$

that calculations of this value require data on the thermal expansion coefficient (γ), molar volume (V), and isothermal compression coefficient (β). When data on elastic crystal properties are partially or completely absent, $C_{d}^{\circ}(T)$ can only be determined approximately. We can, for instance, use the Grüneisen's equation if the β value is not known or the Nernst–Lindemann's equation if the γ and β values are not known.

Because of the absence of the complete set of the data required for calculating $C_{d}(T)$ by Eq. (10), we used Eq. (5) to describe this contribution. It was understood that this approach could give fairly accurate heat capacity values only over a temperature range bounded from above ($T < ~0.5T_{m}$). To remove this limitation, we gave preference to the procedure based on the use of available $C_{p, exp}^{\circ}(T)$ data in the high-temperature range assuming that this procedure is more valid than Grüneisen's or Nernst-Lindemann's approximations.

We assumed that the $C_{d}^{\circ}(T)$ contribution changes over the series of RF₃ compounds largely because of changes in the molar volume, and consequently, we calculated the difference between $C_{p, exp}^{\circ}(T)$ and $C_{p, cal}^{\circ}(T)$ over the temperature range from 600 K to T_{m} (in certain cases, from 600 K to the temperature of the $\beta \rightarrow \alpha$ transition, T_{tr}) and normalized by V_{RF_3} for each lanthanide trifluoride. The values obtained at equal temperatures were averaged. The whole series of average values was then approximated by

the polynomial $(a + bT + cT^2)$. This dependence multiplied by the molar volume of RF₃ constitutes an analytic equation describing the correction $C^{\circ}_{d, \text{ cor}}(T)$ to the heat capacity of the corresponding lanthanide trifluoride. Finally, the heat capacity values calculated by Eq. (9) were corrected by adding the contribution

$$C^{\circ}_{
m d.cor}(T) = V_{
m RF_3} \left(-8.068 \times 10^{-2} + 9.054 \times 10^{-5}T + 5.275 \times 10^{-8}T^2 \right)$$

at all temperatures at which $C_{d, cor}(T)$ values were nonnegative. Note that the $(a + bT + cT^2)$ polynomial was calculated ignoring several $C_{p, exp}(T)$ dependences obtained by Lyon et al. (1978), Charlu et al. (1970), Spedding and Henderson (1971), Spedding et al. (1974), and Lyapunov et al. (2000a, b) because of systematic errors in enthalpy increment measurements.

The heat capacities over the complete temperature range were calculated with the equation

$$C_{\text{p,cal}}^{\circ}(T) = C_{\text{lat}}^{\circ}(T) + C_{\text{exs}}^{\circ}(T) + C_{\text{d,cor}}^{\circ}(T)$$
(11)

by summing three contributions. The first contribution was calculated on the basis of low-temperature heat capacity measurements, the second contribution was estimated from spectral data or data of theoretical calculations of electron excitation energies, and the third contribution was obtained from high-temperature enthalpy increment measurements.

4.1.4 Influence of polymorphic transitions

Calculations of the thermodynamic functions of some lanthanide trifluorides require taking into account the $\beta \rightarrow \alpha$ polymorphic transition characterized by the enthalpy of transition and observed in the temperature dependences of heat capacities.

According to the literature data (Kovács and Konings, 2003), β and α polymorphs exist in the solid state in SmF₃, EuF₃, GdF₃, ErF₃, TmF₃, YbF₃, and LuF₃. The $\Delta_{tr}H^{\circ}$ enthalpy of $\beta \rightarrow \alpha$ transitions in SmF₃, EuF₃, and GdF₃ is fairly low compared with the enthalpy of melting $\Delta_m H^{\circ}$. In the other compounds, $\Delta_{tr}H^{\circ}$ is comparable with $\Delta_m H^{\circ}$ (see Table 13).

According to Spedding and Henderson (1971) and Spedding et al. (1974), heat capacity jumps are observed at the temperatures at which the $\beta \rightarrow \alpha$ transition occurs. However, the presence of such a jump reported by Spedding and Henderson (1971) for HoF₃ was not confirmed by Lyapunov et al. (2000a). The temperature dependence of the heat capacity over the region of the supposed existence of the α polymorph gave a smooth in the temperature range in which Spedding and Henderson (1971) recorded a break. The data on LuF₃ obtained by Spedding and Henderson (1971) and by Lyapunov et al. (2004) differ to a still greater extent. The phase transition (melting) was accompanied by a very substantial heat capacity decrease (Spedding and Henderson, 1971),

R	T _{tr} (K)	⊿ _{tr} H° (kJ∕mol)	<i>Т</i> _т (К)	⊿ _m H° (kJ∕mol)
La	_	-	1766	55.87
Ce	_	-	1703	56.52
Pr	_	-	1670	57.28
Nd	_	-	1649	54.75
Pm	_	-	1605	53.40
Sm	743	1.784	1571	52.43
Eu	973	8.714	1549	52.90
Gd	1347	6.029	1501	52.44
Tb	_	-	1446	58.44
Dy	_	-	1426	58.42
5	1300 ^{<i>a</i>}	2.400^{a}	1430 ^a	54.00 ^{<i>a</i>}
Но	_	-	1416	56.77
	_	-	1418 ^a	56.90 ^a
Er	1388	29.47	1413	27.51
Tm	1325	30.28	1431	28.90
Yb	1267	24.46	1435	29.74
Lu	1230	25.07	1455	29.27

TABLE 13 Temperatures and enthalpies of phase transitions in RF_3 according to Kovácsand Konings (2003)

^{*a*} Data for DyF₃ and HoF₃ were taken from Lyapunov et al. (2000a,b).

whereas in the other study, the heat capacity was found to increase slightly (Lyapunov et al., 2004).

To understand the behavior of the temperature dependence of the heat capacity in the range of phase transitions, let us consider other reports, where volume changes caused by phase transitions were measured (Khairulin et al., 1998a,b, 2000; Stankus et al., 1997, 1999). The data on relative volume changes are presented in Table 14. According to this table, volume changes are insignificant for RF₃ molecules characterized by low enthalpies of the $\beta \rightarrow \alpha$ transition. At the same time, volume changes are noticeably larger in compounds characterized by higher enthalpies of transition. These results are in agreement with the trends in θ_D , θ_{E1} , θ_{E3} , and α variations described above. These parameters experienced a jumpwise increase related to a jumpwise increase in molar volume in passing from one structure to the other.

One more experimental observation described in Stankus et al. (1997, 1999) and Khairulin et al. (1998a,b, 2000) is noteworthy. No well-defined temperature boundary is observed for molar volume variations of several lanthanide trifluorides when the β polymorph is heated to a temperature close to the melting point, and volume growth in the transition to the α

R	$\beta ightarrow lpha$	$\alpha \to \text{liq}$	References
Gd	2.1	16.7	Stankus et al. (1999)
Dy	0	15.5	Khairulin et al. (1998a)
Ho	0	-	Lyapunov et al. (2000a)
Er	16.9	0.75	Khairulin et al. (2000)
Yb	16.6	2.6	Stankus et al. (1997)
Lu	16.4	4.2	Khairulin et al. (1998b)

 TABLE 14
 Relative volume changes (%) in RF3 caused by phase transition

phase occurs gradually. Bearing this in mind, we described the temperature dependence of heat capacity in the region of the existence of the α polymorph by a curve without discontinuity at the $\beta \rightarrow \alpha$ transition temperature. In the majority of cases, the calculated temperature dependence of heat capacity intersected the step dependences observed experimentally in the middle of the temperature interval of the existence of the α polymorph. Reduced Gibbs energy calculations were therefore performed including the enthalpy of $\beta \rightarrow \alpha$ transitions at temperatures corresponding to the beginning of the transitions.

4.1.5 Thermodynamic functions for condensed state

Calculations of thermodynamic functions for the compounds under consideration in the condensed state were performed as follows. To ensure representation in the form of the standard polynomial (Gurvich et al., 1978–1984; IVTANTERMO, 2004)

$$-\frac{[G^{\circ}(T) - H^{\circ}(0)]}{T} = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, \quad (12)$$

where $x = T \times 10^{-4}$,

values of heat capacity found by Eq. (11) were approximated by a polynomial form

$$C_{\rm p}^{\circ}(T) = c_1 + c_2 x^{-2} + c_3 x + c_4 x^2 + c_5 x^3, \tag{13}$$

where $x = T \times 10^{-4}$.

The form of polynomial (13) is such that it allows one to find the values of the f_1 - f_7 coefficients of Eq. (12)

$$f_2 = c_1; f_3 = c_2/2; f_5 = c_3/2; f_6 = c_4/6; f_7 = c_5/12.$$

The f_1 value was calculated from the following equation:

$$S^{\circ}(298) = f_1 + f_2 + f_2 \ln x - f_3 x^{-2} + 2f_5 x + 3f_6 x^2 + 4f_7 x^3, \quad (14)$$

with T = 298.15 K. In turn, the f_4 value was calculated from the equation

$$H^{\circ}(298) - H^{\circ}(0) = 10(f_2x - 2f_3x^{-1} - f_4 + f_5x^2 + 2f_6x^3 + 3f_7x^4)$$
(15)

with the same temperature (298.15 K).

For the calculation of the same factors in the subsequent temperature ranges, the $S^{\circ}(T)$ and $H^{\circ}(T) - H^{\circ}(0)$ values were previously determined at the lower boundary temperature, taking into account the entropy and enthalpy of phase transition. In these calculations, Eqs. (14) and (15) were used with the set of the f_1 - f_7 coefficients found from the temperature dependence of $- [G^{\circ}(T) - H^{\circ}(0)]/T$ in the previous range of temperatures.

The thermodynamic functions were calculated with the $S^{\circ}(298)$ values from Table 12, and the enthalpies and phase transition temperatures listed in Table 13. The missing $C_{p}^{\circ}(\text{liq})$ values were estimated by jointly analyzing data not only on RF₃ but also on RCl₃ taking into account the data on the structure of their melts and of melts of related compounds (Chervonnyi and Chervonnaya, 2007b). This analysis will be presented in detail in describing the thermodynamic functions of RCl₃ in Section 5. Here, we only give the $C_{p}^{\circ}(\text{liq})$ values themselves in J/(mol·K): 153.33 (LaF₃), 154.46 (CeF₃), 155.93 (PrF₃), 154.03 (NdF₃), 152.34 (PmF₃), 151.26 (SmF₃), 148.45 (EuF₃), 137.90 (GdF₃), 141.73 (TbF₃), 137.30 (DyF₃), 132.71 (HoF₃), 129.85 (ErF₃), 128.51 (TmF₃), 125.29 (YbF₃), and 123.73 (LuF₃). Also note that the calculations were performed on the assumption that this characteristic parameter is constant over the whole temperature range T_m -2000 K. The thermodynamic functions are given in Table A5 in the form of the f_i coefficients (see Appendix).

The ultimate goal of this work was the calculation of thermodynamic functions, primarily enthalpies and reduced Gibbs energies used in practical calculations, by the second and third laws of thermodynamics. In view of this, the applicability of the procedure used for heat capacity calculations can be estimated by comparing these thermophysical parameters.

4.1.6 Applicability scope of the method for calculating $C_{p, cal}(T)$

According to the conclusions drawn by Gurvich et al. (1978–1984), it is very difficult and often impossible to select an equation that allows the heat capacity to be satisfactorily calculated over the whole temperature range from T = 0 K to $T_{\rm m}$ (or $T_{\rm tr}$). For this reason, this range is divided into two intervals, 0–298.15 K and 298.15 K– $T_{\rm m}$ (or $T_{\rm tr}$) when processing experimental data. For these intervals, forms of $C_{\rm p}^{\circ}(T)$ description based on separate approximations of $C_{\rm p}^{\circ}, \exp(T)$ were suggested. This approach can be recommended in view of the temperature intervals of the corresponding methods for experimentally determining the heat capacity and high-temperature enthalpy increments. In spite of all the shortcomings (Demlow et al., 1998; Oganov and Dorogokupets, 2004; Oganov et al., 2002) of the quasi-harmonic model as a method for determining the contribution of $C_{p}^{\circ}(T)$ over a wider temperature range (up to $T \approx 0.7T_{m}$). The model provides fairly accurate estimates of the low-temperature heat capacity for RF₃ compounds. This opens up the possibility of sound estimates of $C_{p}^{\circ}(T)$ for compounds not studied experimentally. An analytic form of the function for correcting heat capacity values, $C_{d, cor}(T)$, over the whole temperature range was suggested. The effectiveness of this method is demonstrated in the following paragraph.

For RF_3 , the largest difference between $C_{p, exp}(T)$ and $C_{p, cal}(T)$ is observed for LaF₃ (see Figure 11). For this compound, the relative difference between the experimental and theoretical heat capacities is larger than 3%, that is, exceeds measurement errors in $C_{p, exp}(T)$, only at temperatures $\geq \sim 1200$ K. Corresponding differences between the enthalpies and reduced Gibbs energies calculated using $C_{p, exp}(T)$ and $C_{p, cal}(T)$ were equal to 0.07% and 0.04%, respectively. These values change as the temperature increases as follows (data in %): 1300 K (6.0, 0.45, 0.03), 1400 K (9.5, 1.22, 0), 1500 K (13.6, 2.27, 0.05), 1600 K (18.2, 3.61, 0.13), 1700 K (23.0,



FIGURE 11 High-temperature heat capacity for LaF₃: (1) and (2), calculations by Eqs. (9) and (11), respectively; \bigcirc , determined from the data reported by Lyon et al. (1978); and \bullet , data from Spedding and Henderson (1971). Reproduced from Chervonnyi and Chervonnaya (2007a) with permission from Pleiades Publishing, Ltd.

5.23, 0.25), and 1766 K (26.1, 6.45, 0.36). It follows that, in spite of a noticeable discrepancy between $C_{p, cal}^{\circ}(T)$ and $C_{p, exp}^{\circ}(T)$, the differences between experimental and calculated enthalpies and reduced Gibbs energies are acceptable. Indeed, for LaF₃, the replacement of the thermodynamic functions based on $C_{p, exp}^{\circ}(T)$ with functions calculated using $C_{p, cal}^{\circ}(T)$ changes $\Delta_{sub}H^{\circ}(298)$ by only ~3 kJ/mol (the second law of thermodynamics) and ~0.1 kJ/mol (the third law).

Comparisons at one temperature ($T = T_m$) are given in Tables 15 and 16 for each lanthanide trifluoride. This temperature was selected because the differences between experimental and calculated thermodynamic functions are maximum at this temperature. Moreover, in order to illustrate the maximum deviations obtained, the thermodynamic functions were calculated from the experimental data that differ most from the results of the calculations.

It follows from the data presented in Tables 15 and 16 that, for the majority of RF_3 compounds, the relative differences are comparatively small. They have noticeable values for the heat capacities for only 6 compounds of a total of 14. The reasons for such deviations are largely related to two factors.

	C _p (T)	C [°] _P (<i>T</i>)									
R	a	Ь	c	δ_{abs}	$\delta_{\rm rel}$						
La	169.70	117.31	125.36	44.34	26.1						
Ce	141.30	120.60	127.89	13.41	9.5						
Pr	125.70	124.54	131.40	-5.70	4.5						
Nd	133.99	123.40	129.96	4.03	3.0						
Sm	182.25	124.48	130.47	51.78	28.4						
Eu	150.66	123.20	128.91	21.75	14.4						
Gd	119.44	113.57	118.84	0.60	0.5						
Tb	111.12	119.34	124.13	-13.01	11.7						
Dy	124.59	116.61	121.19	3.40	2.7						
Но	126.32	113.89	118.34	7.98	6.3						
Er	121.89	113.037	117.41	4.48	3.7						
Tm	97.86	113.79	118.24	-20.38	20.8						
Yb	117.39	112.94	117.39	0	0						
Lu	114.50	112.95	117.82	-3.32	2.9						

TABLE 15	Comparison of	[:] the heat ca	pacity of	lanthanide	trifluorides	at $T =$	T_{r}
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^{*a*} Found by experimental data processing.

^b Calculated by Eq. (9).

² Calculated by Eq. (11). The heat capacity values and their absolute differences (δ_{abs}) are in J/(mol·K). All relative differences (δ_{rel}) are in %.

	$H^{\circ}(T) - H^{\circ}(T)$	298)			-[G°(T) - H°(298)]/T					
R	a	Ь	δ_{abs}	$\delta_{\rm rel}$	а	Ь	δ_{abs}	$\delta_{\rm rel}$		
La	172.88	161.73	11.15	6.4	204.282	203.556	0.725	0.4		
Ce	163.44	158.64	4.80	2.9	215.022	214.684	0.338	0.2		
Pr	153.75	156.61	-2.86	1.9	215.370	215.171	0.199	0.1		
Nd	154.27	154.30	0.03	0	214.027	214.068	-0.041	0		
Sm	158.05	149.00	9.05	5.7	208.458	207.497	0.960	0.5		
Eu	171.38	155.36	16.03	9.4	207.776	204.851	2.925	1.4		
Gd	133.10	134.51	-1.42	1.1	197.794	198.063	-0.268	0.1		
Tb	119.96	126.73	-6.76	5.6	196.598	198.408	-1.810	0.9		
Dy	124.85	121.60	3.25	2.6	198.225	197.001	1.224	0.6		
Ho	120.20	118.87	1.33	1.1	196.352	196.173	0.179	0.1		
Er	117.62	115.26	2.36	2.0	194.431	193.269	1.162	0.6		
Tm	150.14	151.27	-1.13	0.8	196.238	194.771	1.467	0.8		
Yb	147.52	145.54	1.98	1.3	192.788	191.096	1.692	0.9		
Lu	146.37	147.85	-1.48	1.0	175.876	176.162	-0.287	0.2		

TABLE 16 Comparison of the enthalpy and reduced Gibbs energy values of lanthanide trifluorides at $T = T_m$

^a Found by experimental data processing.
 ^b The heat capacity values were calculated by Eq. (11). The enthalpy values and their absolute differences (δ_{abs}) are in kJ/mol. The reduced Gibbs energy values and their absolute differences (δ_{abs}) are in J/(mol·K). All relative differences (δ_{rel}) are in %.

First, there is an anomalously rapid increase in heat capacities at $T > 0.5T_{\rm m}$ (LaF₃ and CeF₃). This effect is clearly shown in Figure 11. It was mentioned by several authors (Lyon et al., 1978; Spedding and Henderson, 1971; Spedding et al., 1974) and explained by a contribution to the heat capacity of a component caused by the formation of equilibrium vacancies in the lattice (Lyon et al., 1978). However, earlier data on CeF₃ (Charlu et al., 1970) are at variance with the data reported by Spedding et al. (1974) although close to our calculation results. In addition, the introduction of the vacancy term into the description of the temperature dependence of the enthalpy was considered statistically unwarranted in more recent works on DyF₃ (Lyapunov et al., 2000b) and HoF₃ (Lyapunov et al., 2000a).

The second factor is an exceedingly large heat capacity jump (Spedding et al., 1974) recorded for the $\beta \rightarrow \alpha$ phase transition in SmF₃ and EuF₃, which is at variance with the results presented by the other authors (Khairulin et al., 1998a,b, 2000; Stankus et al., 1997, 1999).

It follows from the results presented in Tables 15 and 16 that, on the whole, the problem of seeking suitable calculation procedures or criteria that allow the reliability of the available experimental data to be estimated and/or missing values to be calculated is, we believe, solved. The main problem was the selection of the method for the optimum interpolation of the lattice heat capacity component. Other models were considered in works dealing with lanthanide compounds and applied in the selection of the interpolation function. For instance, the R atom was treated as a weakly bound localized Einstein oscillator in a fairly rigid crystal lattice described by the Debye model (Bryan et al., 2003; Christensen et al., 2003). There are examples of the use of only the Debye model (Novikov, 2001, 2003; Sirota et al., 2002). A model with one characteristic temperature as an approximation parameter for analyzing and/or predicting thermodynamic properties was also tested (Demlow et al., 1998; Komada and Westrum, 1997; Westrum and Komada, 1986). Note that the form of the interpolation function is usually chosen by minimizing the difference between its values and the corresponding experimental data for a minimum number of variable parameters. We used this principle to select Kelley's equation (Gurvich et al., 1978–1984) and found that as few as four variable parameters were enough to determine their systematic variations over the whole series of lanthanide compounds. Even the presence of a discontinuity in the temperature dependences evidenced by experimental data on some RF3 trifluorides did not prevent us from obtaining the sought values with fairly high accuracy, despite that the theoretical dependence was a smooth function. This is true for RF₃ molecules for which no measurements are available for the low-temperature heat capacity (see Table 12).

Note that the trends in the characteristic parameters used to describe $C_{lat}^{\circ}(T)$ were reproduced in calculations of $C_{exs}^{\circ}(T)$ from the corresponding data on \mathbb{R}^{3+} ions incorporated into the crystal lattice of a diamagnetic compound and on free \mathbb{R}^{3+} ions (see Table 5). The method of calculations substantiated by Chervonnyi and Chervonnaya (2004g) for determining the thermodynamic functions of gaseous compounds was found to be acceptable for solving a similar problem for the condensed state.

A comparison (Chervonnyi and Chervonnaya, 2005a) of the reduced Gibbs energies and enthalpies obtained by us with those from Barin's handbook (Barin, 1995) shows that the relative difference can be as large as 2% for the first parameter and 8% for the second one. The data were compared for LaF₃, CeF₃, PrF₃, NdF₃, EuF₃, GdF₃, DyF₃, and HoF₃. The handbook (Barin, 1995) does not contain data on the other RF₃ compounds.

The reliability of our thermodynamic functions for the condensed state can be further checked by calculating the enthalpies of sublimation from the experimental saturated vapor pressures according to the second and third laws of thermodynamics.

4.2 Calculations of sublimation enthalpy

The enthalpies of sublimation under standard conditions were calculated according to the second and third laws of thermodynamics with the use of the available experimental data on saturated vapor pressures (Bencze et al., 1996; Besenbruch et al., 1967; Biefeld and Eick, 1975, 1976, 1979; Gibson and Haire, 1989; Hildenbrand and Lau, 1995; Kent et al., 1996; Lim and Searcy, 1966; Mar and Searcy, 1967; McCreary and Thorn, 1973a,b, 1974a,b; Petzel and Greis, 1976; Petzel et al., 1992; Roberts and Searcy, 1972; Scinner and Searcy, 1968; Stolyarova et al., 1996; Suvorov et al., 1966; Zmbov and Margrave, 1966a, 1967b, 1968). The data obtained are summarized in Table 17.

The enthalpies of sublimation were calculated by the third law of thermodynamics with the primary data on absolute saturated vapor pressures. For second-law calculations, the $\Delta_{sub}H^{\circ}(T)$ value was determined from the slope of the semilogarithmic plot; *T* was set equal to the mean temperature of measurements.

Second-law calculations of the enthalpy of sublimation of PmF₃ from the (Pr_{1/3}Pm_{1/3}Sm_{1/3})F₃ sample (Gibson and Haire, 1989) give a higher and unrealistic enthalpy value. In our view, third-law calculations provide more reliable results, although the saturated vapor pressure of PmF₃ was determined by comparison with vapor pressure data for PrF₃. According to Gibson and Haire (1989), the ratio between the vapor pressures over praseodymium and promethium trifluorides is 0.7 ± 0.4 at 1573 K. If $\Delta_{sub}H^{\circ}$ (PrF₃, 298) = 439. 1 kJ/mol, the vapor pressure over PmF₃ is

	\varDelta_{sub}	H°(298, II	law)	\varDelta_{sub}	H°(298, II	l law)			$\varDelta_{\sf sub}$	l°(298, II la	w)	$\varDelta_{\sf sub} H$	l°(298, III la	aw)	
R	β	αζ	liq ^d	β ^{<i>b</i>}	ας	liq ^d	References	R	β ^{<i>b</i>}	ας	liq ^d	β ^{<i>b</i>}	αζ	liq ^d	References
La	-	412.4	-	-	449.3	-	Kent et al. (1996)	Gd	-	414.1	-	-		-	Zmbov and Margrave (1968)
	-	368.6	-	-	449.7	-	Suvorov et al. (1966)		-	457.3	-	_	458.3	-	McCreary and Thorn (1973a)
	-	448.0	-	-	442.4	-	Mar and Searcy (1967)	Tb	-	443.5	-	-		-	Zmbov and Margrave (1968)
	-	439.6	-	-	-	-	Skinner and Searcy (1971)		-	451.0	-	-	453.2	-	McCreary and Thorn (1974b)
	-	439.6	-	-	-	-	Roberts and Searcy (1972)	Dy	-	471.9	445.1	-	451.2	444.5	Besenbruch et al. (1967)
	-	450.8	-	-	445.0	-	Petzel et al. (1992)		-	468.1	-	-	457.3	-	Zmbov and Margrave (1968)
	-	438.2	-	-	443.6	-	Hildenbrand and Lau (1995)		-	454.1	-	-	454.9	-	McCreary and Thorn (1974a)
Ce	-	422.3	-	-	431.0	-	Lim and Searcy (1966)		-	450.9	-	-	454.7	-	Stolyarova et al. (1996)
	-	407.1	-	-	430.9	-	Suvorov et al. (1966)	Но	-	468.2	439.2	-	450.0	451.3	Besenbruch et al. (1967)
	-	409.7	-	-	-	-	Zmbov and Margrave (1968)		-	446.9	-	-	452.8	-	Zmbov and Margrave (1968)

TABLE 17 Enthalpies of sublimation for RF_3 (kJ/mol)^a

	-	434.2	-	-	-	-	Roberts and Searcy (1972)		-	462.3	-	-	458.2	-	McCreary and Thorn (1974a)
	-	438.6	-	-	439.6	-	McCreary and Thorn (1973b)	Er	511.2	393.5	461.9	455.3	454.5	454.4	Besenbruch et al. (1967)
Pr	-	375.2	-	-	439.2	-	Suvorov et al. (1966)		458.1	-	-	457.7	-	-	McCreary and Thorn (1974a)
	-	435.8	-	-	439.1	-	Scinner and Searcy (1968)		458.2	442.6	452.6	457.2	456.1	457.0	Bencze et al. (1996)
	-	417.4	-	-		-	Zmbov and Margrave (1968)	Tm	-	431.6	-	-	445.8	-	Zmbov and Margrave (1967b)
Nd	-	388.7	-	-	432.8	-	Zmbov and Margrave (1966a)		-	432.5	453.1	-	447.9	447.7	Biefeld and Eick (1976)
	-	370.1	-	-	449.7	-	Suvorov et al. (1966)		501.2	487.3	450.7	454.8	453.7	452.4	Bencze et al. (1996)
	-	439.9	-	-	444.8	-	McCreary and Thorn (1974b)	Yb	-	408.6	-	-	439.9		Zmbov and Margrave (1967b)
Pm	-	482.1	-	-	445.5	-	Gibson and Haire (1989)		-	-	-	-	-	456.0	Biefeld and Eick (1975)
Sm	-	436.2		-		-	Zmbov and Margrave (1968)		-	-	439.6	-	-	457.9	Petzel and Greis (1976)
	-	438.1	424.8	-	435.0	-	Biefeld and Eick (1979)	Lu	453.1	429.1	-	439.9	442.6	-	Zmbov and Margrave (1967b)
Eu	-	384.9	-	-		-	Zmbov and Margrave (1968)		464.7	464.7	-	458.2	463.4	-	Petzel et al. (1992)

 a Calculations from saturated vapor pressures over the $^{b}\beta$ phase, $^{c}\alpha$ phase, and d melt, respectively.

 6.48×10^{-5} atm. Third-law calculations of the enthalpy of sublimation of this compound subsequently give 445.5 kJ/mol.

Third-law calculations of the enthalpy of sublimation of DyF_3 from the data reported by Stolyarova et al. (1996) were performed only taking into account the saturated vapor pressures found by the authors at separate temperatures by two methods (with the use of a reference and by isothermal vaporization).

Analysis of data in Table 17 shows that the difference between the values obtained according to the second and third laws of thermodynamics lies within several kJ/mol in the majority of cases, although there are also strongly different values. This is characteristic of the results from earlier mass spectrometric measurements used to determine the thermodynamic characteristics of vaporization of these compounds (Kent et al., 1996; Zmbov and Margrave, 1966a, 1967b, 1968). These data, however, seem to be quite reliable for SmF₃ and EuF₃. Similar discrepancies between the enthalpies of sublimation were obtained in processing the data reported by Suvorov et al. (1966), Mar and Searcy (1967), and, in part, Besenbruch et al. (1967). Calculations of the enthalpies of sublimation from the certified data of McCreary and Thorn (1973a,b, 1974a,b) on CeF₃, NdF₃, GdF₃, TbF₃, DyF₃, HoF₃, and ErF₃, however, show that the use of the thermodynamic functions suggested by us results in a difference of \sim 4 kJ/mol in two cases and 0.4–2.2 kJ/mol for the remaining five compounds. Similar results were obtained with the data obtained by Hildenbrand and Lau (1995) on LaF₃, Scinner and Searcy (1968) on PrF₃ and SmF₃, Biefeld and Eick (1976) on TmF₃, Stolyarova et al. (1996) on DyF₃, and Petzel and Greis (1976) on LuF₃.

In addition, the enthalpies of sublimation found by second- or thirdlaw calculations for LaF₃ (Mar and Searcy, 1967; Petzel et al., 1992; Roberts and Searcy, 1972; Skinner and Searcy, 1971), CeF₃ (Roberts and Searcy, 1972), PrF₃ (Suvorov et al., 1966), SmF₃ (Zmbov and Margrave, 1968), DyF₃ (Besenbruch et al., 1967; Zmbov and Margrave, 1968), and ErF₃ (Bencze et al., 1996; Besenbruch et al., 1967) agree with the corresponding values mentioned above to within the specified limits. Also note that the data of Biefeld and Eick (1975) and Petzel and Greis (1976) found according to the third law of thermodynamics differ by as little as 1.9 kJ/mol, although agreement between the second-law values is much worse. These contradictions are, however, not surprising, considering the complexity of saturated pressure measurements for ytterbium trifluoride and, also, samarium and europium trifluorides (see, for instance, Biefeld and Eick, 1975).

Here, it is appropriate to show in a graphical form (Figure 12) the differences in $\Delta_{sub}H^{\circ}(298)$ values which are recommended according to our analysis and data from Myers and Graves (1977b) and Kovács and Konings (2003).



FIGURE 12 Enthalpies of sublimation of lanthanide trifluorides: ▲, data from Kovács and Konings (2003); ●, data from Myers and Graves (1977b); and ○, data determined in this work.

4.3 Reference data for lanthanide trifluorides

The enthalpies of sublimation recommended by us are summarized in Table 18 for standard temperature 298.15 K.

The data obtained allowed us to calculate the atomization energies of gaseous lanthanide trifluorides using the enthalpies of formation of lanthanides themselves and atomic fluorine from IVTANTERMO (2004) as well as the enthalpies of formation of crystalline lanthanide trifluorides from Kovács and Konings (2003), as the reliability of the latter data is beyond doubt. The enthalpies of formation and of atomization are collected in Table 18.

To summarize, the applicability of our thermodynamic functions to practical calculations is proved by comparing the enthalpies of sublimation found according to the second and third laws of thermodynamics under standard conditions. This can generate objection, because fairly accurate absolute saturated vapor pressures and their temperature dependences can rarely be simultaneously obtained experimentally. For the compounds under consideration, however, this comparison was the only way of proving the validity of our approach in view of the absence of experimental data obtained by other methods. The main point is that the close agreement between the $\Delta_{sub}H^{\circ}(298)$ values obtained according to the second and third laws of thermodynamics is by no means fortuitous. McCreary and Thorn (1973a,b, 1974a,b) tested the reliability of their own

R	⊿ _{sub} H°(298) ^a	⊿ _f H°(cr, 298) ^b	⊿ _f H°(g, 298)	⊿ _{at} H°(298)
La	443.6	-1699.5 ± 2.0	-1255.9	1924.0
Ce	439.6	-1689.2 ± 5.0	-1249.6	1904.8
Pr	439.1	-1689.1 ± 2.6	-1250.0	1844.0
Nd	444.8	-1679.4 ± 1.9	-1234.6	1799.9
Pm	445.5	-1675 ± 20	-1229.5	1726.8
Sm	435.0	-1700.7 ± 5.0	-1265.7	1709.4
Eu	384.9	-1611.5 ± 5.0	-1226.6	1640.9
Gd	458.3	-1699.3 ± 2.3	-1241.0	1877.7
Tb	453.2	-1695.9 ± 5.0	-1242.7	1866.9
Dy	454.9	-1692.0 ± 1.9	-1237.1	1760.5
Ho	458.2	-1697.8 ± 2.3	-1239.6	1777.9
Er	457.7	-1693.6 ± 1.9	-1235.9	1787.9
Tm	453.7	-1693.7 ± 5.0	-1240.0	1710.9
Yb	456.9	-1655.1 ± 5.0	-1198.2	1588.8
Lu	458.2	-1679.9 ± 5.0	- 1221.7	1887.7

 TABLE 18
 Recommended enthalpies of sublimation, enthalpies of formation and enthalpies of atomization for lanthanide trifluorides (kJ/mol)

^{*a*} Chervonnyi and Chervonnaya (2007a).

^b Kovács and Konings (2003). The error in the enthalpies was estimated as ± 3 kJ/mol.

and literature data on the temperature dependence of saturated vapor pressure in order to reveal systematic errors. The absence of such errors was convincingly documented in (McCreary and Thorn, 1974a), where, indeed, a linear dependence of $\Delta_{sub}S^{\circ}(T)$ on $\Delta_{sub}H^{\circ}(T)$ was obtained. According to Thorn (1970), linear dependences confirm the absence of such errors in the enthalpies of sublimation (vaporization) calculated according to the second law of thermodynamics.

Close agreement between experimental and calculated $\Delta_{sub}H^{\circ}(298)$ values and small differences in the case of the enthalpies and Gibbs energies was obtained for the majority of RF₃ compounds. This is not only evidence of the effectiveness of the method for calculating heat capacities. The thermodynamic characteristics obtained can furthermore be recommended for thermodynamic modeling of equilibria with the participation of these compounds. The experience of calculation and estimation of the corresponding thermophysical parameters accumulated during the investigation of RF₃ compounds can be transferred to other classes of related compounds. We shall show this in the forthcoming sections, for the example for RCl₃ and RCl₂.

The data reported in Table 18 allowed us to recalculate them for a standard temperature of 0 K using the needed parameters from IVTANTERMO (2004). These enthalpies are summarized in Table 19.

R	⊿ _{sub} H°(0)	$\Delta_{\rm f} H^{\circ}$ (cr, 0)	$\varDelta_{\rm f} H^{\circ}$ (g, 0)	⊿ _{at} H°(0)
La	443.027	-1696.334	-1253.307	1915.475
Ce	438.939	-1684.937	-1245.998	1896.823
Pr	438.353	-1686.305	-1247.952	1836.777
Nd	444.005	-1676.365	-1232.360	1792.185
Pm	443.580	-1670.696	-1227.116	1718.941
Sm	433.974	-1696.625	-1262.651	1699.476
Eu	383.833	-1607.922	-1224.089	1633.914
Gd	457.188	-1692.777	-1235.589	1867.414
Tb	452.048	-1690.555	-1238.507	1858.332
Dy	453.698	-1686.599	-1232.901	1752.726
Ho	456.931	-1692.843	-1235.912	1769.737
Er	456.432	-1689.514	-1233.082	1779.907
Tm	452.389	-1690.404	-1238.015	1703.840
Yb	455.591	-1651.510	-1195.919	1580.744
Lu	456.904	-1675.649	-1218.745	1878.570

TABLE 19 Recommended enthalpies of sublimation, enthalpies of formation, andenthalpies of atomization at 0 K (in kJ/mol)^a

^a All primary (experimental) enthalpy values are given with an accuracy of 0.1 kJ/mol. Other values calculated from them have an accuracy of 0.001 kJ/mol, as accepted in IVTANTERMO (2004).

5. THERMODYNAMIC FUNCTIONS FOR LANTHANIDE TRICHLORIDES IN CONDENSED STATE

In the previous section, we tested a procedure for calculating heat capacity over a broad temperature range, up to the melting point, based on analysis of experimental low-temperature heat capacities. High-temperature enthalpy increment measurements were used to correct the calculated $C_{p, cal}^{\circ}(T)$ values at temperatures $T > \sim 0.5T_{m}$. We found that the use of this procedure for calculating the thermodynamic functions for lanthanide trifluorides gave satisfying results. A comparison of the standard enthalpies of sublimation $\Delta_{sub}H^{\circ}(298)$ calculated by the second and third laws of thermodynamics showed that the thermodynamic functions give a correct description of equilibria involving these compounds.

In this section, we aim at calculating the thermodynamic functions for lanthanide trichlorides RCl_3 (R = La–Lu) using the procedure suggested in the previous section for determining the thermophysical parameters of RF_3 .

The temperature dependence of heat capacity over the temperature range T = 0 to $T_{\rm m}$ or $T_{\rm tr}$ was written as the sum of three contributions (see Eq. (11)). Two of these ($C_{\rm lat}(T)$ and $C_{\rm d, \ cor}(T)$) were described analytically

by successively treating the experimental low-temperature heat capacity and high-temperature enthalpy increment data. The third contribution $(C_{exs}^{\circ}(T))$ was calculated by the classic scheme from the selected electronic excitation energies of the compounds under consideration (see Table 2).

At the first stage, the $C_{exs}^{\circ}(T)$ contribution was subtracted, if necessary, from the low-temperature heat capacity values. The set of $C_{lat}^{\circ}(T)$ data obtained in this way was approximated by the method of least squares using Eq. (6) that describes the contribution of the lattice heat capacity in the quasi-harmonic approximation. As a result, we calculated the values of the θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α variable parameter. We then determined the analytic dependence of changes in these parameters on the molar volume *V*. This allowed us to estimate the θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α parameters for unstudied compounds.

At the second stage, the sum of $C_{lat}^{\circ}(T)$ and $C_{exs}^{\circ}(T)$ was calculated for each compound at a given temperature or over a temperature interval.

The $C_{d, cor}(T)$ contribution that removes temperature limitations of the quasi-harmonic model used to determine $C_{lat}(T)$ was described at the third stage of calculations. The analytic form of $C_{d, cor}(T)$ was found by comparing $C_{p, cal}(T)$ and $C_{p, exp}(T)$; $C_{p, exp}(T)$ values were calculated from the experimental high-temperature enthalpy increments.

The final stage of calculations repeated the second step, but the summation was performed with the inclusion of the three contributions present in Eq. (11).

Similar step-by-step calculations of intermediate and final results were used to describe the temperature dependence of the heat capacity of lanthanide trichlorides.

It was shown in the previous section that the characteristic parameters used to describe the lattice heat capacity component consistently changed depending on the molar volume of compounds. This dependence was individual in character within the same crystal structure type. Lanthanide trichlorides are known to crystallize in three different space groups. The hexagonal structure of the UCl₃ type with CN 9 is characteristic of lanthanum through gadolinium trichlorides. Terbium trichloride adopts a PuBr₃-type orthorhombic structure with CN = 8, and the other lanthanide trichlorides have lattices similar to the YCl₃ monoclinic crystal lattice with CN = 6. Taking this into account, we looked for trends in the characteristic parameters of two groups of RCl₃ crystallizing in hexagonal and monoclinic space groups. This processing, however, gave contradictory results for the characteristic parameters of monoclinic compounds, which prompted us to perform a search for additional proofs of the applicability of the data listed in Table 2 to $C_{exs}^{\circ}(T)$ calculations. The results obtained are considered below separately for each type of compounds with similar crystal structures.

5.1 Hexagonal trichlorides

The characteristic parameters presented in Table 20 were obtained by the method of least squares from the θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α , values found in approximating the experimental data (Landau et al., 1973; Sommers and Westrum, 1976, 1977; Varsanyi and Maita, 1965) by linear dependences (see Figure 13).

The accuracy of these calculations was controlled using χ^2 parameter values determined as

$$\chi^2 = \frac{\left\{\sum_{i=1}^n \left[C_p^\circ(T_i) - C_{p,\text{est}}^\circ(T_i)\right]^2\right\}}{n-1}$$

where $C_p^{\circ}(T_i)$ are the values to be approximated, $C_{p, \text{ est}}^{\circ}(T_i)$ are the values calculated by the approximating equation, *n* is the number of experimental values to be approximated, and χ^2 is in $J^2/(K \cdot \text{mol})^2$.

Let us consider the application of approximating procedures to selected experimental data.

R	V _{RCl,} (cm³∕mol)	Θ_{D} (K)	$\Theta_{E1} (cm^{-1})$	$\Theta_{E2}(cm^{-1})$	$\Theta_{E3}(cm^{-1})$	α × 10 ⁶ (mol∕J)
La	63.74	145.35253	156.20000	188.70969	227.67852	1.32021
Ce	62.46	145.94210	156.77792	189.88063	232.52652	1.33663
Pr	61.40	146.43026	157.25624	190.85019	236.54136	1.35022
Nd	60.56	146.81710	157.63529	191.61852	239.72293	1.36100
Pm	59.99	147.07961	157.89250	192.13989	241.88185	1.36831
Sm	59.30	147.39737	158.20387	192.77102	244.49528	1.37715
Eu	58.64	147.70124	158.50140	193.37457	246.99517	1.38561
Gd	58.39	147.81645	158.6145	193.60337	247.94197	1.38882
Tb	57.67	148.14803	158.9394	194.26194	250.66903	1.39806
Dy	74.89	139.51764	150.76888	177.81107	185.04690	1.15019
Ho	73.52	140.14856	151.38709	179.06419	190.23589	1.16776
Er	72.58	140.58146	151.81127	179.92399	193.79621	1.17981
Tm	71.88	140.90383	152.12714	180.56426	196.44752	1.18879
Yb	70.91	141.35055	152.56485	181.45150	200.12147	1.20123
Lu	70.69	141.45186	152.66413	181.65273	200.95474	1.20405

TABLE 20 Molar volumes and characteristic parameters for calculating the lattice contribution to the heat capacity of lanthanide trichlorides^{*a*}

^{*a*} The values given are vibrational frequencies rather than the Einstein characteristic temperatures; these frequencies can conveniently be compared with those of IR and Raman bands. The conversion of frequencies to characteristic temperatures is performed using a multiplier of 1.43879 K•cm.



FIGURE 13 Dependence of the $\theta_{\rm D}$ values on molar volume in the series of RCl₃ compounds.

Calculations of the characteristic parameters for diamagnetic LaCl₃ were performed by jointly processing experimental data (Landau et al., 1973; Sommers and Westrum, 1976; Varsanyi and Maita, 1965) obtained over the temperature ranges 1.59–4.16, 5.63–347.26, and 2–20 K, respectively. Although we combined the results of three different experiments, the approximating function was characterized by a fairly low χ^2 (0.03146). This approach allowed us to refine the θ_D values.

The experimental data on EuCl₃ (Sommers and Westrum, 1977), namely 59 values over the temperature range 4.95–346.44 K, were processed, and $\chi^2 = 0.02263$ was obtained. The absence of ground-state level ⁷F₀ splitting and the presence of the ⁷F₁, ⁷F₂, and ⁷F₃ levels situated fairly high in energy for europium trichloride allow the characteristic parameters to be calculated from the low-temperature data (Sommers and Westrum, 1977) without preliminarily subtraction of the $C_{exs}^{\circ}(T)$ contribution. Indeed, processing 16 values from Sommers and Westrum (1977) over the temperature range 4.95–24.68 K gave a lower χ^2 value (0.00344).

The θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α values for GdCl₃ that fell on the corresponding rectilinear dependences on the molar volume were obtained by approximating $C_{p,exp}^{\circ}(T)$ from the data reported by Sommers and Westrum (1977) at temperatures above 50 K, resulting in $\chi^2 = 0.04569$. This was related to the phase transition from the paramagnetic disordered to ferromagnetic ordered state. According to Hovi et al. (1970), this transition occurs at 2.20 K. Sommers and Westrum (1977) assumed that the shape of the $C_{p,exp}^{\circ}(T)$ peak was characterized by a

short temperature interval of ordering above the Curie point and considered their first three $C_{p, exp}^{\circ}(T)$ values at the lowest temperatures as being erroneous. They calculated the entropy and enthalpy increments between 4.2 and 9 K after combining their data with the results reported by Wolf et al. (1961), Wyatt (1963), and Marquard (1967). However, the interval of ordering mentioned above is likely not very short. Bryan et al. (2003) investigated Eu₄Ga₈Ge₁₆ and found that the magnetic ordering of Eu²⁺ (which is isostructural with Gd³⁺) extended up to 35–40 K. Calculations of the lattice contribution of the heat capacity of GdCl₃ by Eq. (6) with the use of the θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α values gives a $C_{p, cal}^{\circ}(T)$ curve that lies below the experimental data (Sommers and Westrum, 1977) over the temperature range 4.9–20.83 K. This lends support to the suggestion that the temperature interval of magnetic ordering of GdCl₃ is broader than it was assumed earlier.

The applicability of the data listed in Table 2 to calculations of $C_{exs}^{\circ}(T)$ for the series of compounds under consideration was checked by processing the data from Sommers and Westrum (1976, 1977) by two different procedures. First, the low-temperature data were fitted to Eq. (8), in which the variable parameters were θ_D , α , and electronic excited state energies closest to zero level, leading to $\chi^2 = 0.00709$. This showed that the zero level is situated at 28.8 cm⁻¹ for PrCl₃, which is lower by 4.3 cm⁻¹ than the usual value. Because of the vicinity of the components of the NdCl₃ doublets, with mean energies 115.39 and 121.21 cm⁻¹, the initial portion of the curve was approximated by varying the energy of the first doublet, for which 93 cm⁻¹ was obtained with a confidence parameter $\chi^2 = 0.09237$.

Next, we approximated the $(C_{p, exp}(T) - C_{lat}(T))$ difference over the whole temperature range of $C_{p, exp}(T)$ measurements by Eq. (7) which describes the $C_{exs}(T)$ contribution and in which variable parameters were some electronic excitation energies ε_i . The $C_{lat}(T)$ values were calculated by Eq. (6) using the characteristic parameters listed in Table 20.

For instance, for neodymium trichloride, we varied the energies of four doublets of the ${}^{4}I_{9/2}$ state, which gave $\chi^{2} = 0.05695$. For europium trichloride, the ${}^{7}F_{1}$ triplet state energy (369.5 cm⁻¹) was varied ($\chi^{2} = 0.01775$). The other excitation energy levels remained unchanged (see Table 2). The ε_{i} values obtained by applying the approximation procedure coincided fairly closely, especially for EuCl₃, with the data from Table 2, the difference between the corresponding values being only 0.5 cm⁻¹. The plots that illustrate the application of this procedure to the data from Sommers and Westrum (1976, 1977) are displayed in Figures 14 and 15.

The $C_p^{\circ}(298)$ and $S^{\circ}(298)$ values were calculated for all the hexagonal lanthanide trichlorides and orthorhombic terbium trichlorides with values of θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α given in Table 20 and data listed in



FIGURE 14 Excess contribution to the heat capacity of NdCl₃: \bigcirc , calculated from the difference between the values measured experimentally (Sommers and Westrum, 1976) and found by Eq. (6); solid line, approximating curve. Reproduced from Chervonnyi and Chervonnaya (2007b) with permission from Pleiades Publishing, Ltd.



FIGURE 15 Excess contribution to the heat capacity of $EuCl_3$: \bigcirc , calculated from the difference between the values measured experimentally (Sommers and Westrum, 1977) and found by Eq. (6); solid line, approximating curve. Reproduced from Chervonnyi and Chervonnaya (2007b) with permission from Pleiades Publishing, Ltd.

Table 2. TbCl₃ was included into this series because of the similarity of V_{TbCl_3} and V_{GdCl_3} values (see Table 20) in spite of the different crystal structures of TbCl₃ and GdCl₃.

Calculated and experimental heat capacities and entropies under standard conditions are summarized in Table 21. Comparison of these values for the series of RCl₃ compounds (R = La-Tb) shows that, on the whole, the suggested calculation procedure yields $C_p^{\circ}(298)$ and $S^{\circ}(298)$ values fairly close to the experimental ones. The corresponding differences lie, as a rule, in the range 0.05–0.82 J/(mol·K). Deviations from calculated values are larger (~1 J/(mol·K)) only for the experimental entropy of PrCl₃ (Sommers and Westrum, 1976) and estimated entropy of CeCl₃ (Sommers and Westrum, 1976).

In summary, the procedure suggested by Chervonnyi and Chervonnaya (2007a) for calculating $C_p(T)$ from the experimental low-temperature heat capacity data for hexagonal RCl₃ results in the same trends in variations of the characteristic parameter as those obtained for RF₃. Two important facts should be mentioned. First, the characteristic temperatures of all the hexagonal lanthanide trichlorides vary in the series $\theta_D < \theta_{E1} < \theta_{E2} < \theta_{E3}$. Second, each of the characteristic parameters decreases linearly as the molar volume increases. Prior to turning to the results of the calculation for monoclinic RCl₃, recall that, for RF₃, the θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α parameters experience a discontinuity when the structure of the crystal lattice changes (Chervonnyi and Chervonnaya, 2007a).

5.2 Monoclinic trichlorides

Attempts at calculating the characteristic parameters for this structural group of RCl₃ compounds were made in processing the experimental data from Gorbunov et al. (1986) and Tolmach et al. (1987c, 1988, 1990b,c,d) on DyCl₃, HoCl₃, ErCl₃, TmCl₃, YbCl₃, and LuCl₃ obtained over the temperature range \sim 8–300 K. Calculations according to the scheme described above, however, gave contradictory results. Let us consider several examples.

The heat capacities of LuCl₃ measured experimentally and smoothed by a cubic spline function were reported by Tolmach et al. (1987c). We calculated θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α on the basis of all these experimental data, except three values in the temperature range 254.24–262.41 K. The characteristic parameters listed in Table 22 were obtained at a comparatively low $\chi^2 = 0.05497$ value. Comparison with the corresponding data on hexagonal lanthanide trichlorides shows that an increase in the molar volume causes an insignificant decrease in α , noticeable increases in θ_{E2} and θ_{E3} , and substantial decreases in θ_D and θ_{E1} . Such modifications of these parameters change the temperature dependence of heat capacity in a quite definite way. Namely, because of the low θ_D and θ_{E1} values, heat

	C _p (298)	S°(298)	S [°] _{exs} (298)	C _P (298)	S [°] _{lat} (298)	S°(298)	
R	Experimental		Calculated				
La	98.03 ^{<i>a</i>}	137.57 ^a	0	97.81	137.90	137.90	
Ce	_	$(150.62)^{b}$	14.716	98.11	137.10	151.83	
Pr	98.95 ^a	153.30 ^{<i>a</i>}	17.884	98.46	136.46	154.34	
Nd	99.24 ^{<i>a</i>}	153.43 ^a	18.312	99.40	135.95	154.25	
Pm	_	$(154.81)^{b}$	17.983	98.74	135.61	153.57	
Sm	99.54^{b}	150.12 ^b	15.255	99.45	135.20	150.47	
Eu	106.98 ^b	144.06 ^b	9.369	106.93	134.81	144.18	
Gd	97.78 ^b	151.42 ^b	17.289	97.42	134.66	151.95	
Tb	_	_	21.165	97.76	134.24	155.38	
Dy	100.5 ± 0.2^{c}	169.6 ± 0.5^{c} ; 176.6 ^d	22.827	98.90	145.76	168.60	
Ho	101.9 ± 0.2^{e}	170.1 ± 0.3^e	23.093	99.28	144.76	167.86	
Er	99.78 ± 0.2^{f}	168.1 ± 0.3^{f}	22.626	99.15	144.08	166.71	
Tm	100.0 ± 0.1^{8}	166.5 ± 0.2^{8}	20.867	99.23	143.58	164.47	
Yb	101.4 ± 0.2^{h}	163.5 ± 0.6^h ; 170.3 ^d	16.572	99.49	142.90	159.48	
Lu	96.62 ± 0.2^c	153.0 ± 0.53^{c}	0	98.23	142.75	142.75	

TABLE 21 $C^{\circ}_{p}(298)$ and $S^{\circ}(298)$ values in J/(mol·K) for lanthanide trichlorides

^{*a*} Sommers and Westrum (1976). ^{*b*} Sommers and Westrum (1977). ^{*c*} Tolmach et al. (1987c). ^{*d*} Tolmach et al. (1988). $S_{lat}^{\circ}(298)$ was obtained by integrating the $C_{lat}^{\circ}(T)/T$ ratio over the temperature range 0–298.15 K, and $C_{lat}^{\circ}(T)$ was calculated by Eq. (6) using the characteristic parameter values obtained. ^{*e*} Tolmach et al. (1990d). ^{*f*} Tolmach et al. (1990b). ^{*g*} Tolmach et al. (1990c). ^{*h*} Gorbunov et al. (1986).

R	θ _D (K)	$ heta_{ extsf{E1}}$ (cm $^{-1}$)	$ heta_{ t E2}$ (cm $^{-1}$)	$ heta_{E3}$ (cm $^{-1}$)	α × 10 ⁶ (mol∕J)	Note
Y	89.9986 ± 0.70856	$\begin{array}{c} 110.67927 \pm \\ 1.08397 \end{array}$	$212.23653 \pm \\ 3.4889$	$\begin{array}{r} 284.92762 \pm \\ 3.78776 \end{array}$	$\begin{array}{r} 1.83940 \pm \\ 0.03346 \end{array}$	Calculations based on data from Tolmach et al. (1990a)
Yb	84.39124	110.71848	196.09755	295.00	1.25121	Estimate based on data from Gorbunov et al. (1986)
Lu	$\begin{array}{r} 84.53918 \pm \\ 0.47736 \end{array}$	$\begin{array}{c} 110.72611 \pm \\ 1.07950 \end{array}$	$\begin{array}{r} 197.20166 \pm \\ 2.79025 \end{array}$	294.3969 ± 3.1172	$\begin{array}{c} 1.20405 \pm \\ 0.04022 \end{array}$	Calculations based on data from Tolmach et al. (1987c)

TABLE 22 Debye characteristic temperature, Einstein oscillator frequencies, and α for YCl₃, YbCl₃, and LuCl₃



FIGURE 16 Temperature dependence of heat capacity of (\Box) LaCl₃ (Sommers and Westrum, 1976), (Δ) GdCl₃ (Sommers and Westrum, 1977), and (\bullet) LuCl₃ (Gorbunov et al., 1986).

capacities below 100 K are noticeably higher than the corresponding values for $LaCl_3$ and $GdCl_3$ (see Figure 16).

Such a behavior of $C_p(T)$ at T < 100 K was not observed for the crystalline lanthanide trichloride hydrates RCl₃·6H₂O (Spedding et al., 1972), oxides R₂O₃ (Gruber et al., 1982; Justice and Westrum, 1963a; Justice et al., 1969), hydroxides R(OH)₃ (Chirico and Westrum, 1980a; Chirico et al., 1981), and trifluorides RF₃ (Flotow and O'Hare, 1981) (see Figure 17). The molar volumes of all lutetium compounds are, however, lower than those of the corresponding gadolinium compounds. There is an example of inverse ratio between the molar volumes, namely, the molar volumes of sulfides are 74.92 for γ -La₂S₃, 66.51 for γ -Gd₂S₃, and 71.31 cm³/mol for ε -Lu₂S₃. According to Westrum et al. (1989) and Gruber et al. (1993), this ratio between the molar volumes insignificantly increases the heat capacity of ε -Lu₂S₃ compared with γ -Gd₂S₃ at temperatures below 100 K. On the other hand, the heat capacity of ε -Lu₂S₃ becomes smaller than that of γ -Gd₂S₃ as the temperature increases above 100 K.

IR and Raman spectral data (Asawa et al., 1968; Basile et al., 1971; Berreman and Unterwald, 1968; Cohen and Moos, 1967a,b; Cohen et al., 1968; Morrison et al., 2000; Murphy et al., 1964; Varsanyi, 1965) on lanthanide trichlorides lead us to suggest that the characteristic Debye temperature decreases because of the lowering of acoustic and low-frequency



FIGURE 17 Temperature dependence of heat capacity of (\Box) LaF₃ (Lyon et al., 1978), (Δ) GdF₃ (Flotow and O'Hare, 1981), and (\bullet) LuF₃ (Flotow and O'Hare, 1981).

optical lattice vibrations of monoclinic lutetium trichloride compared with hexagonal lanthanum and gadolinium trichlorides, however, to a lesser degree than according to the results obtained by Tolmach et al. (1987c).

We decided to check the reliability of the characteristic parameters determined from the heat capacity of LuCl₃ by calculating them for isostructural YCl₃ for which experimental data were reported by Tolmach et al. (1990a). This compound has a molar volume (74.78 cm³/ mol) approximately equal to that of DyCl₃. If the θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α parameters changed consistently for YCl₃ and LuCl₃, it would be possible to estimate these parameters for the other monoclinic lanthanide trichlorides and then determine the $C_{exs}^{\circ}(T)$ component of their heat capacities. We found that the experimental data for YCl₃ (Tolmach et al., 1990a) could be approximated by Eq. (6) with a low $\chi^2 = 0.05636$ value. As far as the characteristic parameters obtained are concerned, it follows from Table 22 that only θ_{E1} and θ_{E3} decrease, as expected, in going from LuCl₃ to YCl₃. All the other parameters increase, and the α parameter increase most substantially, by a factor of ~1.5.

One more contradiction should be mentioned concerning the results obtained for monoclinic trichlorides. Tolmach et al. (1988) proved the consistency of the experimental heat capacities of YbCl₃ (Gorbunov et al., 1986) and LuCl₃ (Tolmach et al., 1987c) by describing the difference

of the heat capacities with the use of the equation for calculating the excess contribution of Schottky's anomaly to the heat capacity of ytterbium trichloride. According to the authors, this difference was in agreement with the calculated value, with the assumption that the electronic ground term of YbCl₃ is split into five Kramers doublets with energies 0, 160, 320, 450, and 640 cm⁻¹.

The ground state of Yb³⁺ (²F_{7/2}), however, splits in the ligand field into four doublets only, and the energy of the next excited electronic state (²F_{5/2}) is 10,214 cm⁻¹ (Martin et al., 1978). Supposing that an inaccuracy slipped in the paper of Tolmach et al. (1988), we calculated the contribution $C_{exs}^{\circ}(T) = C_{p}^{\circ}(T) - C_{lat}^{\circ}(T)$ to the experimental heat capacities (Gorbunov et al., 1986) of YbCl₃. The $C_{lat}^{\circ}(T)$ value was found according to Eq. (6) by substituting the θ_D , θ_{E1} , θ_{E2} , θ_{E3} , and α values into this equation. The latter were estimated with the assumption of a linear dependence on the molar volume, similar to the one obtained for the characteristic parameters of LuCl₃ and determined by processing the experimental data (Tolmach et al., 1987c). Subsequent calculations showed that this contribution did coincide with the calculated $C_{exs}^{\circ}(T)$ curve (see Figure 18) if the electronic state energies and the statistical



FIGURE 18 Excess contribution to the heat capacity of $YbCl_3$: O, calculated from the difference between the values measured experimentally in Gorbunov et al. (1986) and found by Eq. (6); \bullet , calculated from the data listed in Table 2; and solid line, approximating curve. Reproduced from Chervonnyi and Chervonnaya (2007b) with permission from Pleiades Publishing, Ltd.

weights from Gorbunov et al. (1986) were used. Calculations of $C_{exs}(T)$ from the data accepted in this work (Table 2), however, give a noticeably different curve (see Figure 18).

Similar phenomena are observed in processing the experimental data for DyCl₃, HoCl₃, ErCl₃, and TmCl₃ (Tolmach et al., 1987c, 1990b,c,d). As for YbCl₃, the $C_{exs}^{\circ}(T) = C_{p}^{\circ}(T) - C_{lat}^{\circ}(T)$ difference curves found from the experimental $C_{p}^{\circ}(T)$ and calculated $C_{lat}^{\circ}(T)$ values do not coincide with those obtained according to the classic theory with the use of the data from Table 2. The $C_{exs}^{\circ}(T)$ curve maxima obtained on the basis of the experimental data are, as a rule, shifted to higher temperatures, and the curves themselves have distorted shapes.

The special features of the characteristic parameters of monoclinic RCl_3 and YCl_3 revealed in the approximation of the experimental data (Gorbunov et al., 1986; Tolmach et al., 1987c, 1988, 1990b,c,d), which differ from those found for hexagonal RCl_3 and the whole series of RF_3 (Chervonnyi and Chervonnaya, 2007a), are likely related to systematic errors in experimental heat capacity measurements. For this reason, our subsequent calculations on monoclinic lanthanide trichlorides were made using the following estimates.

We suggested that the rules established for changes in the characteristic parameters depending on the molar volume remain valid for monoclinic lanthanide trichlorides. It was assumed as a first approximation that the dependence of θ_D , θ_{F1} , θ_{F2} , θ_{F3} , and α parameters on the molar volume lies on the same straight lines for the whole series of lanthanide trichlorides. This allowed us to determine their values, which were then used as a basis for calculating thermodynamic functions. The results were applied to calculate the enthalpies of sublimation according to the second and third laws of thermodynamics from the literature data on saturated vapor pressures. Agreement between these results was checked. Next, the characteristic parameters were stepwise decreased for compounds of the series DyCl₃-LuCl₃, and the thermodynamic functions were again calculated and used to determine the enthalpies of sublimation. This procedure was repeated until the total difference between the enthalpies of sublimation found using the second and third laws of thermodynamics became minimum. Simultaneously, attention was given to agreement between the enthalpies of sublimation obtained using the third law of thermodynamics and similar values determined from independent measurements. Note that a decrease in the characteristic parameters most strongly influences the standard entropies of compounds $S^{\circ}(298)$, and therefore, through the reduced Gibbs energy values, the enthalpy of sublimation found according to the third law of thermodynamics. This means that agreement between the enthalpies is largely attained as a result of a decrease in $\Delta_{\rm sub}H^{\circ}(298, \text{III law})$ rather than an increase in $\Delta_{\rm sub}H^{\circ}(298, \text{II law})$. The characteristic parameters obtained by the method of successive approximations for the DyCl₃–LuCl₃ compounds are listed in Table 20. An example of the analytic dependence of the characteristic parameter on molar volume is shown in Figure 13.

Note that our estimates of the characteristic parameters for the monoclinic group of compounds yielded smaller values compared with the corresponding data on hexagonal RCl₃. As with RF₃, we observe a jumptype change in these parameters when the crystal structure changes. As a result, we found that the ratio between the $C_{p,cal}^{\circ}(T)$ values of GdCl₃ and LuCl₃ in the temperature range 0–350 K is similar to the ratio between the heat capacities calculated for γ -Gd₂S₃ and ϵ -Lu₂S₃ (Gruber et al., 1993; Westrum et al., 1989).

Calculated and experimental (Gorbunov et al., 1986; Tolmach et al., 1987c, 1988, 1990b,c,d) heat capacity and entropy values under standard conditions are summarized in Table 21. We see that calculated $C_p^{\circ}(298)$ values differ by $\sim 1-3$ J/(mol·K) from the experimental data for Dy–Yb trichlorides. As far as $S^{\circ}(298)$ is concerned, our calculations give values that are lower by $\sim 1-10$ J/(mol·K) than those reported by Gorbunov et al. (1986) and Tolmach et al. (1987c, 1990c,b,d). Taking into account the corrections (Tolmach et al., 1988) introduced into the experimental data for DyCl₃ and YbCl₃ (Gorbunov et al., 1986; Tolmach et al., 1987c), the difference between calculated and experimental $S^{\circ}(298)$ values for these lanthanide trichlorides becomes as large as $\sim 8-11$ J/(mol·K).

5.3 Determination of the $C_{d, cor}^{\circ}(T)$ contribution

We compared the $C_{p, cal}^{\circ}(T)$ and $C_{p, exp}^{\circ}(T)$ values to investigate the origin of the systematic underestimation of the $C_{p, cal}^{\circ}(T)$ data at high temperature ($T > \sim 0.5T_{m}$). This underestimation is caused by the use of the quasi-harmonic approximation for calculating the contribution of lattice heat capacity. The $C_{p, exp}^{\circ}(T)$ values were obtained from high-temperature heat capacity measurements by differential scanning calorimetry or enthalpy increments determined by drop calorimetry for the whole series of RCl₃ compounds except PmCl₃, ErCl₃, YbCl₃, and LuCl₃ (Dworkin and Bredig, 1963a,b; 1971; Gaune-Escard et al., 1996; Reuter and Seifert, 1994; Rycerz and Gaune-Escard, 2002a,b,c; Walden and Smith, 1961).

The smallest difference between $C_{p, exp}^{\circ}(T)$ and $C_{p, exp}^{\circ}(T)$ occurs for GdCl₃ with $C_{p, exp}^{\circ}(T)$ values calculated from the Dworkin–Bredig's dependence (Dworkin and Bredig, 1971) for $H^{\circ}(T) - H^{\circ}(298)$ over the temperature range 298–875 K (see Figure 19). This example can be considered ideal for proving the agreement between calculated values and experimental data over the overlapping temperature range because the mean relative difference between $C_{p, exp}^{\circ}(T)$ and $C_{p, cal}^{\circ}(T)$ in the range T = 298.15-520 K then does not exceed 0.1%. In the next temperature interval, the difference between $C_{p, exp}^{\circ}(T)$ and $C_{p, cal}^{\circ}(T)$ increases



FIGURE 19 High-temperature heat capacity data for $GdCl_3$: (1) and (2), calculations by Eqs. (9) and (11), respectively; (\bigcirc) determined from the data reported in Dworkin and Bredig (1971).

monotonically. We used these data to determine the contribution $C_{d, cor}(T)$ for the whole series of lanthanide trichlorides. For this purpose, the difference between $C_{p, exp}(T)$ and $C_{p, cal}(T)$ heat capacities of GdCl₃ above \sim 520 K was normalized by the molar volume of GdCl₃ and approximated by the polynomial ($a + bT + cT^2$). The dependence obtained multiplied by the molar volume of RCl₃ represented an analytic equation that described the correction $C_{d, cor}(T)$ to the heat capacity of the corresponding lanthanide trichloride,

 $C^{\circ}_{d \text{ cor}}(T) = V_{\text{RCl}_3} \left(-5.82875 \times 10^{-2} + 5.17212 \times 10^{-5} T + 1.39131 \times 10^{-7} T^2 \right).$

This correction was used to calculate the heat capacity according to Eq. (11) over the whole temperature range at all *T* at which $C^{\circ}_{d,cor}(T)$ was positive.

Comparison of 16 $C_{p,exp}^{\circ}(T)$ high-temperature measurements (Dworkin and Bredig, 1963a,b, 1971; Gaune-Escard et al., 1996; Reuter and Seifert, 1994; Rycerz and Gaune-Escard, 2002a,b,c; Walden and Smith, 1961) with the corresponding $C_{p, cal}^{\circ}(T)$ values calculated by Eq. (11) for 11 lanthanide trichlorides shows that the relative difference between these values does not exhibit sharp peaks. On the whole, it oscillates within an even narrower interval of values than the corresponding difference for RF₃. At 400 K, there are only four compounds, LaCl₃, CeCl₃, NdCl₃ (Gaune-Escard et al., 1996),
and EuCl₃ (Rycerz and Gaune-Escard, 2002b) for which the relative difference between $C_{p, \exp}^{\circ}(T)$ and $C_{p, cal}^{\circ}(T)$ is larger than 3%. At $T = T_{m}$, the number of such compounds increases to 10, but the maximum relative difference for them does not exceed 15%. This ensures a correct description of the temperature dependence of heat capacity that can be used in thermodynamic function calculations (Chervonnyi and Chervonnaya, 2007a).

Interestingly, according to the dependence of the characteristic parameters in the series of monoclinic RCl₃, which was established on the basis of the results obtained by Gorbunov et al. (1986) and Tolmach et al. (1987c, 1988, 1990b,c,d), we should observe an additional increase in $C_{\rm p, cal}^{\circ}(T)$ at $T > \sim 0.7T_{\rm m}$ because of the increase in $\Theta_{\rm E2}$ and $\Theta_{\rm E3}$ and, accordingly, the decrease in $\Theta_{\rm D}$ and $\Theta_{\rm E1}$. This would increase the relative difference between $C_{\rm p, exp}^{\circ}(T)$ and $C_{\rm p, cal}^{\circ}(T)$.

5.4 Temperatures and enthalpies of phase transitions

The enthalpies of phase transitions for lanthanide trichlorides were determined experimentally several times. A selection of these data can be found, for instance, in the Gmelin Handbook (1982) or in the review by Kovács and Konings (2003), which also contains values recommended by the authors. These data and the results reported in Goryushkin et al. (1990b), Laptev (1996), Laptev and Kiseleva (1994), which were not cited in the above reviews, are summarized in Table 23. The table also contains data from Barin (1995) for comparison. In addition, we deemed it necessary to cite the results of systematic studies of phase transition parameters performed by Gaune-Escard et al. (1996), Rycerz and Gaune-Escard (2002a,b) which were cited in the review by Kovács and Konings (2003).

Note the special feature in the works of Goryushkin et al. (1990b), Laptev (1996), and Laptev and Kiseleva (1994). In these studies, thermal decomposition of the lanthanide trichlorides was prevented by placing quartz capillaries with carbon tetrachloride into quartz ampullae with samples. Above 500 °C, carbon tetrachloride decomposed and released chlorine. Phase transitions were therefore performed in the atmosphere that, in the authors' view, ensured congruent melting of the samples studied. The data obtained are characterized by systematic exaggeration of the phase transition temperatures compared with those reported earlier (Gmelin Handbook, 1982). The spread of the reported melting points can be as large as $\pm 30^{\circ}$. For this reason, these data must be examined on the basis of a criterion that allows the most reliable values to be selected.

The reliability of melting point determinations and estimates can most easily be judged upon using the entropies of melting ($\Delta_m S^\circ$). Dworkin and Bredig (1971) noted that there exists a correlation between the crystal structure of lanthanide chlorides and $\Delta_m S^\circ$ (or the sum of the entropies of polymorphic transition and melting). According to their data, the

		T _{tr} or T _m	$\Delta_{ m tr} {m {\cal H}^\circ} \; { m or} \ \Delta_{ m m} {m {\cal H}^\circ}$	T _{tr} or T _m	$\Delta_{ m tr} {m {\cal H}^\circ} { m or} \ \Delta_{ m m} {m {\cal H}^\circ}$	T _{tr} or T _m	$\Delta_{ extsf{tr}} extsf{H}^\circ ~ extsf{or} \ \Delta_{ extsf{m}} extsf{H}^\circ$	T _{tr} or T _m	$\Delta_{ extsf{tr}} extsf{H}^\circ$ or $\Delta_{ extsf{m}} extsf{H}^\circ$	T _{tr} or T _m	$\Delta_{tr} \mathcal{H}^\circ$ or $\Delta_{m} \mathcal{H}^\circ$
R	Transition	а		Ь		с		d		е	
La	$\alpha \to liq$	1147	59.7	_	-	1127	55.7	1131	54.392	1135 ^f	55.7
Ce	$\alpha \rightarrow liq$	1105	51.5	-	-	1086	55.5	1080	53.137	1090 ⁸	55.5
Pr	$\alpha \rightarrow liq$	1072	49.9	-	-	1061	52.1	1059	50.626	1061	52.1
Nd	$\alpha \rightarrow liq$	1049	51.2	-	_	1032	48.1	1032	50.208	1032	48.1
Pm	$\alpha \rightarrow liq$	-	_	-	_	-	_	-	_	994 ⁸	47.8
Sm	$\alpha \rightarrow liq$	955	45.0	-	_	950	47.6	950	46.024	950	47.6
Eu	$\alpha \rightarrow liq$	906	52.4	-	_	894	45.0	897	51.045	894	45.0
Gd	$\alpha \rightarrow liq$	-	_	886	60.3	873	40.6	875	40.71	873	40.6
Tb	eta ightarrow lpha	-	_	793	23.1	790	13.8	783	14.079	783	14.079
	$\alpha \to liq$	-	_	857	31.6	854	20.8	855	19.351	855	19.351
Dy	$\beta ightarrow lpha$	-	_	929	36.5	611	1.4	924	25.522	611	1.4
-	$\alpha \rightarrow liq$	-	_	-	_	909	22.8	-	_	909	22.8
Но	$\alpha \rightarrow liq$	-	_	1014	37.9	-	_	993	30.648	993 ^h	30.543 ^h
Er	$\beta ightarrow lpha$	-	_	1064	38.5	1025	5.3	1049	32.635	1025	5.3
	$\alpha \rightarrow liq$	-	_	-	_	1046	31.1	-	_	1046	31.1
Tm	$\alpha \rightarrow liq$	-	_	1110	46.9	1092	35.6	-	_	1092	35.6
Yb	$\alpha \rightarrow liq$	1148	63.6	1156	58.1	-	_	-	_	1127 ⁱ	35.982 ⁱ
Lu	$\alpha \to liq$	_	-	1179	59.3	_	_	-	-	1198 ^j	39.33 ^j

TABLE 23 Phase transition temperatures (K) and phase transition enthalpies (kJ/mol) for lanthanide trichlorides

^a Laptev and Kiseleva (1994) and Laptev (1996).
^b Goryushkin et al. (1990b).
^c Gaune-Escard et al. (1994, 1996) and Rycerz and Gaune-Escard (2002a,b).
^d Values used by Barin (1995) for calculating thermodynamic functions.
^e Data used in our calculations of thermodynamic functions.
^f Savin et al. (1979).
^g Data recommended by Kovács and Konings (2003).
^h Dworkin and Bredig (1971) and Spedding and Daane (1960).
ⁱ Drobot et al. (1968), Jantsch et al. (1931), and Kojima and Kikuchi (1953).
^j Kojima and Kikuchi (1953) and Spedding and Daane (1960).

entropies of melting of hexagonal RCl₃ and orthorhombic TbCl₃ are $50 \pm 4 \text{ J/(mol} \cdot \text{K})$. The corresponding values for monoclinic RCl₃ approximately equal to 31 J/(mol \cdot K).

According to Tosi et al. (1991), the mechanisms of melting could be classified according to three main types, each correlating with chemical bonds in three different structures. This interrelation was later described analytically by Akdeniz and Tosi (1992) on the basis of the conclusions drawn by Tallon and Robinson (1982). The relation between $\Delta_m S^\circ$ and the ratio between molar volume changes caused by melting and the molar volume itself ($\Delta V/V$) in the form applicable to lanthanide trichlorides,

$$\Delta_{\rm m}S^{\circ} = R \left[5.0\ln(2) + 12.4\frac{\Delta V}{\rm V} \right] \tag{16}$$

actually describes the correlations observed by Dworkin and Bredig (1971).

The density of packing in a crystal is determined as the ratio between the sum of the volumes of ions in a unit cell and the volume of the unit cell itself. According to Peterson (1995), the density of packing in a crystal increases in going from six-coordinate monoclinic structures to eightcoordinate orthorhombic structures, the hexagonal structures with ninecoordinate cations being intermediate. The more compact orthorhombic and hexagonal structures are characterized by the largest volume changes upon melting, which distinguishes them from monoclinic structures, for which these changes are much smaller. As concerns the temperature of melting, this parameter decreases fairly smoothly at the beginning of the series (R = La-Tb) and equally smoothly increases at the end of the series (R = Dy-Lu).

In order to employ Eq. (16) for calculating the entropy of phase transitions, we used the experimental ΔV values for RCl₃ (Iwadate et al., 1995; Wasse and Salmon, 1999a,b) to interpolate the ΔV values with respect to the molar volume V for all lanthanide trichlorides. This was done separately for R = La–Tb and Dy–Lu. The $\Delta V/V$ values calculated in this way (Table 24) were used to determine the entropies of phase transitions, which played the role of reference values for comparison with similar characteristics found by measuring the temperature and enthalpy of melting. Here and throughout, if two phase transitions are observed experimentally (TbCl₃, DyCl₃, and ErCl₃), the sum of the entropies of these transitions, $\Delta_{tr}S^{\circ} + \Delta_{m}S^{\circ}$, is taken into account.

Comparative analysis shows that all the temperatures of melting found experimentally (Goryushkin et al., 1990b; Laptev, 1996; Laptev and Kiseleva, 1994) have higher values. Higher values were also reported for the enthalpies of melting of LaCl₃, EuCl₃, and YbCl₃ by Laptev (1996) and of all the compounds studied in Laptev and Kiseleva (1994). As a

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R	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	ть
∆V/V (%)	15.3	18.0	20.1	21.9	23.1	24.5	25.8	26.4	27.8
R	Dy	Но	Er	Tm	Yb	Lu	u		_
∆V/V (%)	0.3	2.9	4.7	6.0	7.9	8	.3		_

TABLE 24 Change in molar volume for lanthanide trichlorides at the temperature of phase transition $\alpha \rightarrow liq$

result, the entropies found from the data obtained in Goryushkin et al. (1990b), Laptev (1996), and Laptev and Kiseleva (1994) are larger than the reference values.

As far as the results obtained by Gaune-Escard et al. (1996) and Rycerz and Gaune-Escard (2002a.b) are concerned, although these values are somewhat lower than the reference values, they should be given preference for three reasons. First, they are close to the results obtained by Barin (1995) and, therefore, agree with the experimental values (Dworkin and Bredig, 1963a,b, 1971; Seifert and Sandrock, 1991a,b; Seifert et al., 1985, 1987, 1988a,b) available at the time when the handbook (Barin, 1995) was compiled. Next, these data more clearly reveal the rule set by Eq. (16). Lastly, the measurements performed (Gaune-Escard et al., 1996; Rycerz and Gaune-Escard, 2002a,b) allowed the expected polymorphic transitions of DyCl₃ and ErCl₃ not observed by Goryushkin et al. (1990b) to be revealed.

Of course, Eq. (16) is approximate and cannot be used to calculate the entropies of phase transitions. It is useful from the point of view of the selection of more reliable experimental data because it shows the tendency of parameter variations in the series of compounds under consideration. We used this equation to select several phase transition parameters not reported by Gaune-Escard et al. (1996) and Rycerz and Gaune-Escard (2002a.b,c) from the set of data available in the Gmelin Handbook (1982). These data included experimental values reported for TbCl₃ (Dworkin and Bredig, 1971), HoCl₃ ($T_m = 993$ K, Drobot et al., 1968; $\Delta_{\rm m}H^{\circ} = 30.543$ kJ/mol, Dworkin and Bredig, 1971), YbCl₃ ($T_{\rm m} = 1127$ K, Jantsch et al., 1931; Drobot et al., 1968; $\Delta_m H^\circ = 35.982 \text{ kJ/mol}$, Kojima and Kikuchi, 1953), and LuCl₃ ($T_m = 1198$ K, Spedding and Daane, 1960; $\Delta_{\rm m}H^{\circ}$ = 39. 33 kJ/mol, Kojima and Kikuchi, 1953). Besides, we consider $T_{\rm m} = 1135$ K being a more comprehensible value (Savin et al., 1979) for LaCl₃ with $\Delta_m H^\circ = 55.7$ kJ/mol (Gaune-Escard et al., 1994). It appears that we must agree with the recommendation by Kovács and Konings (2003), who suggested a somewhat higher temperature of melting for

CeCl₃ (1090 K), and with their estimate of the temperature of melting of PmCl₃ (994 K). At the same time, we suggest a somewhat higher value for the enthalpy of melting $\Delta_m H^\circ$ for PmCl₃ (48.7 kJ/mol).

Newer data on the temperatures of melting of some lanthanide trichlorides, 1023 K for ErCl₃, 1094 K for TmCl₃, 1133 K for YbCl₃, and 1165 K for LuCl₃ (Bűchel and Seifert, 1999) as well as 1145 K for LaCl₃, 1104 K for CeCl₃, 1062 K for PrCl₃, 1037 K for NdCl₃, 941 K for SmCl₃, 893 K for EuCl₃, and 878 K for GdCl₃ (Seifert, 2002), are in agreement with our selection of these parameters for calculations. Exceptions are data on LaCl₃ and CeCl₃, which are close to those reported by Laptev (1996) and Laptev and Kiseleva (1994), and LuCl₃, whose melting point is lower than that reported by Goryushkin et al. (1990b).

5.5 Heat capacity in liquid state

The available experimental data on $C_p^{\circ}(\text{RCl}_3,\text{liq})$ were obtained either by drop calorimetry measurements of $H^{\circ}(T) - H^{\circ}(298)$ or by differential scanning calorimetry with the use of suitable references. Both methods give fairly high instrumental accuracy (1–3%) (Jacobson et al., 1999). Nevertheless, analysis of the whole series of results obtained does not reveal patterns in the variation of heat capacity for the series of lanthanide trichlorides unless additional data on $C_p^{\circ}(\text{RF}_3,\text{liq})$, the structure of the liquid phase formed in melting, and the influence of the excess contribution of the excited electronic states of molecules on the heat capacity values are taken into account.

Indeed, among available the experimental data in Gaune-Escard et al. (1994), Rycerz and Gaune-Escard (2002a,b,c), Dworkin and Bredig (1963a, b, 1971), Savin et al. (1979), and Savin and Mikhailova (1981), we come across heat capacity values for the same lanthanide trichloride that differ by 25% from each other (see Table 25). A similar picture is observed for the $C_{\rm p}^{\circ}({\rm RF}_3,{\rm liq})$ values (Lyapunov et al., 2000a,b, 2004; Spedding and Henderson, 1971; Spedding et al., 1974) (see Table 26). Even if we ignore the unreliable heat capacity value for LaF₃ (Spedding and Henderson, 1971), which is approximately two times larger than the values for the other lanthanide trifluorides, attention is attracted by the spread of the data for DyF₃, within a range of 14% (Lyapunov et al., 2000b; Spedding et al., 1974), and for HoF₃ for which differences larger than 30% between heat capacitiy data occur (Lyapunov et al., 2000a; Spedding and Henderson, 1971). Finally, we note that Spedding and Henderson (1971) have proposed a noticeable correction to the heat capacity of GdF₃ when this parameter was repeatedly measured (Spedding et al., 1974). The tendency of trichlorides to decompose at high temperatures (especially in the liquid state) was already mentioned by Chervonnyi and Chervonnaya (2004a). As concerns lanthanide trifluorides, their high

R	r (Å)	$C_{\rm exs}^{\circ}(T_{\rm m})^{a}$	C _p (liq)			
La	1.032	0	157.74 ^b , 196.1 ^c	157.737 ^d	157.7 ^e	142.50 ^f
Ce	1.010	4.48	165.0 ⁸	159.829 ^d	161.05 ^e	146.27 ^f
Pr	0.990	5.65	133.89 ^b , 155.28 ^h , 185.2 ^c	133.888 ^d	155.3 ^e	146.78 ^f
Nd	0.983	6.01	146.44 ^b , 149.53 ^h , 177.9 ^g	146.44 ^d	149.5 ^e	146.89 ^f
Pm	0.970	6.83	_	_	(147) ^e	147.26 ^f
Sm	0.958	8.32	145.26 ⁱ	142.256 ^d	144.4 ^e	148.30 ^f
Eu	0.947	10.39	155.96 ^j	142.256 ^d	(142) ^e	150.00 ^f
Gd	0.938	0	141.00 ^k , 139.50 ^l , 139.89 ^h	139.515 ^d	139.7 ^e	139.26 ^f
Tb	0.923	3.76	144.5 ^l , 139.27 ^m	144.474^{d}	144.47 ^e	142.44 ^f
Dy	0.912	1.14	144.77 ^l , 159.43 ^h	144.766 ^d	144.77 ^e	144.77 ^f
Ho	0.901	0.38	147.70 ^k , 148.67 ^l	143.511 ^d	148.67 ^e	143.47 ^f
Er	0.890	0.16	141.00^{k}	141.001 ^d	141.00 ^e	142.70 ^f
Tm	0.880	0.30	-	_	(141) ^e	142.32 ^f
Yb	0.868	0.11	-	_	$(140)^{e}$	141.50 ^f
Lu	0.861	0	-	-	(141) ^e	141.01 ^f

TABLE 25 Heat capacity in $J/(mol \cdot K)$ of RCl_3 in the liquid state

^{*a*} The second column contains the smoothed crystal radius values (Shannon, 1976) for the \mathbb{R}^{3+} ions (CN = 6). $C_{ess}^{ess}(T_m)$ is the excess contribution to heat capacity at the temperature of melting. ^{*b*} Dworkin and Bredig (1963a).

^c Savin et al. (1979).

^d Data from Barin (1995) with references to Pankratz (1984).

^e Data recommended by Kovács and Konings (2003).

^f Data recommended by Chervonnyi and Chervonnaya (2007b). The value for CeCl₃ is recommended taking into account the result obtained by King and Christensen (1959).

⁸ Savin and Mikhailova (1981).

^h Gaune-Escard et al. (1996).

^{*i*} Rycerz and Gaune-Escard (2002c).

^j Rycerz and Gaune-Escard (2002b).

^k Dworkin and Bredig (1963b). ¹ Dworkin and Bredig (1971).

^m Rycerz and Gaune-Escard (2002a).

activity in interactions with container materials in the molten state is well known. In our view, these are the factors that are responsible for the large spread of experimental data.

Sometimes, this spread is so large, and the heat capacity values are so contradictory, that preference is given to estimates rather than experimental data for the calculation of thermodynamic parameters recommended in handbooks. The results of the analysis performed by Pankratz (1984), which were used by Barin (1995), substantiate the aforesaid statement (see Tables 25 and 26).

R	$C_{\rm exs}^{\circ}(T_{\rm m})^{a}$	$C_{\rho}^{\circ}(liq)$			
La	0	337.73 ^b	167.36 ^c	135 ^d	153.33 ^e
Ce	4.26	125.02 ^f	133.88 ^c	130.61 ^d	154.46 ^e
Pr	8.71	130.75 ^b	130.75 [°]	130.76 ^d	155.93 ^e
Nd	7.88	172.76 ^b	172.775 [°]	172.82 ^d	154.03 ^e
Pm	8.21	-	_	_	152.34 ^e
Sm	10.05	148.95 ^f	_	148.94 ^d	151.26 ^e
Eu	9.05	-	_	_	148.45 ^e
Gd	0	117.08 ^b , 127.82 ^f	127.821 [°]	115.20 ^d	137.90 ^e
Tb	6.41	151.92 ^f	_	151.91 ^d	141.73 ^e
Dy	3.92	156.90 ^f , 137.4 ^g	156.90 [°]	156.92 ^d	137.30 ^e
Ho	1.32	95.98 ^b , 138.5 ^h	96.013 ^c	135.02 ^d	132.71 ^e
Er	0.50	139.12 ^f	139.118 [°]	146.83 ^d	129.85 ^e
Tm	1.06	140.33 ^f	140.336 [°]	140.32 ^d	128.51 ^e
Yb	0.17	121.71 ^f	_	121.70 ^d	125.29 ^e
Lu	0	104.18 ^b , 131.8 ⁱ	-	126.94 ^d	123.73 ^e

TABLE 26 Heat capacity in $J/(mol \cdot K)$ of RF₃ in the liquid state

 $\stackrel{a}{\cdot} C^{\circ}_{exs}(T_m)$ is the excess contribution to heat capacity at the temperature of melting.

^b Spedding and Henderson (1971).

^c Data from Barin (1995) with reference to Pankratz (1984).

^{*d*} Data recommended by Kovács and Konings (2003).

^e Data recommended by Chervonnyi and Chervonnaya (2007b).

^f Spedding et al. (1974).

^{*g*} Lyapunov et al. (2000b). ^{*h*} Lyapunov et al. (2000a).

^{*i*} Lyapunov et al. (2004).

In our view, the construction of various correlation dependences for the parameter under consideration requires taking into account the influence of excess heat capacity caused by the presence of excited electronic states. We used the excited state energies and statistical weights given above to calculate the temperature dependence of the excess heat capacity over the temperature ranges 0-1200 K for RCl₃ and 0-1700 K for RF₃. Although the curves obtained were similar with respect to the corresponding terms for the two series of compounds, they had singularities within the series of lanthanides itself that should be mentioned.

Because of the energy separation of levels with their intrinsic statistical weights for compounds of the first half of the series (Ce-Eu), a noticeable second maximum appears at temperatures close to melting points. This maximum increases in going from cerium to europium. As far as the second half of the series is concerned (Tb-Yb), the $C_{exs}^{\circ}(T_m)$ value smoothly decreases from terbium to ytterbium (see Figure 20).

The dependence of the heat capacity of solids under standard conditions (298 K) on the atomic numbers of lanthanides is a smooth curve for



FIGURE 20 Dependence of C_{exs} upon temperature for some lanthanide trifluorides.

each half of the lanthanide series. The shape of this curve is determined by $C_{exs}^{\circ}(T_m)$ variations. Even the substantial deviation for europium compounds is determined by just the value of this contribution. We believe that the correlation equations for the heat capacity of liquid RF₃ and RCl₃ at their melting points are governed to a substantial extent by the $C_{exs}^{\circ}(T_m)$ value. The $C_{exs}^{\circ}(T_m)$ contributions calculated by us at the temperatures of melting are listed in Tables 25 and 26.

The other rules governing changes in the heat capacity of the liquid state should be sought on the basis of the structural data on molten substances.

The local structure of a molten lanthanide trichloride was studied for the first time by Maroni et al. (1974) who investigated the LaCl₃–KCl binary mixture. The conclusion of the existence of at least one highly symmetrical associated species in this melt based on the analysis of Raman spectra was soon substantiated in the case of yttrium trichloride (Papatheodorou, 1977). In the latter work, the high-symmetry structural unit was identified as the octahedral hexachloride (YCl₆)^{3–}. Next, a comparison of the Raman spectra of liquid and solid yttrium trichloride samples led the authors to conclude that lattice-type vibrations occurred in melts.

Numerous subsequent works on pure lanthanide trichlorides and various binary mixtures were performed by X-ray diffraction (Igarashi et al., 1990; Iwadate et al., 1994; Mochinaga et al., 1991a, 1993a,b), Raman spectroscopy (Chrissanthopoulos and Papatheodorou, 2000; Fukushima et al., 1999; Matsuoka et al., 1993; Mochinaga et al., 1993a; Photiadis et al., 1998), and neutron diffraction (Martin et al., 2002; Wasse and Salmon, 1997, 1999a,b; Wasse et al., 2000). They substantiated that the local structure is predominantly determined by the octahedral species mentioned above. Globally, $(RCl_6)^{3-}$ octahedra form a loose network and are connected with each other by one or two bridging bonds. The same conclusion follows from electrical conductivity measurements (Fukushima et al., 1991, 1995b, 1996, 1997; Iwadate et al., 1999a; Mochinaga et al., 1991b; Wasse and Salmon, 1999a) and determinations of the molar volumes of melts (Fukushima et al., 1995a; Igarashi and Mochinaga, 1987; Iwadate et al., 1999b). It was substantiated theoretically by simulations of the melt structure (Hutchinson et al., 1999, 2001; Iwadate et al., 1999c; Takagi et al., 1999).

The concept of the structure of melts built from a loose network comprising separate layers with weak interlayer interactions between distorted octahedra leads us to suggest that the heat capacity of melts can, as a first approximation, be represented as the sum of the lattice contribution of the liquid $C_{lat}(liq)$ and excess heat capacity contribution $C_{exs}^{\circ}(T_m)$. The prediction of the $C_{lat}(liq)$ dependence within the series of lanthanide trichlorides and a comparison of the corresponding dependences for similar compounds can then be performed using data on the vibrational frequencies of the $(RX_6)^{3-}$ octahedra. According to Photiadis et al. (1998), within groups of compounds of the same type, these frequencies depend linearly on the polarizing power of the central cation q/r, where q is the charge of the cation and r is its radius.

Indeed, if the characteristic $v_l(A_{1g})$ vibration frequencies of $(RF_6)^{3-}$ octahedra measured by Dracopoulos et al. (1998) for lanthanum, cerium, neodymium, samarium, dysprosium, and ytterbium are plotted versus the inverse ionic radii of the cations (Shannon, 1976), it becomes clear that the data in the selected system of coordinates can be represented in the form of linear dependences describing variations in $v_l(A_{1g})$ separately, according to the classification of RF₃ structures (R = La–Pm and Sm–Lu).

Similar data on lanthanide trichlorides were only obtained for hexagonal LaCl₃ (Photiadis et al., 1993/1994), NdCl₃ (Photiadis et al., 1998), and SmCl₃ (Fukushima et al., 1999). The $v_l(A_{1g})$ frequencies of the $(RCl_6)^{3-}$ octahedra formed in the melts of monoclinic RCl₃ (R = Dy–Lu) can be estimated using the corresponding data on YF₃ (Dracopoulos et al., 1997) and YCl₃ (Papatheodorou, 1977).

It follows from the ionic radii values (Shannon, 1976) smoothed by a polynomial of degree 2 that the ionic radius of Y^{3+} is between those of Dy^{3+} and Er^{3+} , and the $v_l(A_{1g})$ value for $(YF_6)^{3-}$ well fits into the straight line that describes changes in the vibrational frequency over the series of orthorhombic RF_3 (R = Sm-Lu). It can therefore be suggested that the $v_l(A_{1g})$ value for octahedral $(YCl_6)^{3-}$ should also lie on the straight line

that describes the ionic radius dependence of this frequency for $(\text{RCl}_6)^{3-}$ octahedra formed by monoclinic RCl_3 (R = Dy–Lu). The corresponding set of straight lines is shown in Figure 21. According to this figure, the characteristic vibrational frequencies in melts of the monoclinic trichlorides RCl_3 (as distinct from those of orthorhombic RF_3) are lower than those of the hexagonal RCl_3 compounds.

These trends in $v_{l}(A_{1g})$ variations depending on the polarizing power of the R³⁺ cation characteristic of liquid lanthanide trifluorides and trichlorides should also be expected for the other spectroscopically recorded vibrations. This, for instance, follows from the Raman spectra of Cs₂NaRBr₆ (R = La, Nd, and Gd) compounds (Photiadis et al., 1998). It was shown that the $v_{l}(A_{1g})$ and $v_{5}(F_{2g})$ vibrations of the (RBr₆)³⁻ octahedron active in Raman and the translational lattice vibration $v_{lat}(F_{2g})$ frequency increase monotonically from the lanthanum- to gadoliniumcontaining compound. The same follows from a comparison of the Raman spectra of NdCl₃ACl (A = Li, Na, K, and Cs) (Photiadis et al., 1998) and SmCl₃ACl (A = Li, Na, and K) (Fukushima et al., 1999).

Variations in the vibrational frequencies of $(RX_6)^{3-}$ octahedra should be similar in character to variations in the lattice contribution $C_{lat}(liq)$ to the heat capacity of melts of compounds of the same type. The only difference is that $C_{lat}(liq)$ decreases while the frequencies increase. Such



FIGURE 21 Dependences of the $v_l(A_{1g})$ vibrational frequencies of $(RX_6)^{3-}$ octahedra on the inverse ionic radius of six-coordinate R^{3+} . Reproduced from Chervonnyi and Chervonnaya (2007b) with permission from Pleiades Publishing, Ltd.

dependences are, however, almost unnoticeable at high temperatures. Moreover, they should not cause well-defined jump-type changes in the heat capacity in going from one polymorph to another, as is clearly seen when we consider the experimental data on lanthanide trifluorides. To understand this phenomenon, let us discuss additional data on the structure of melts.

In several publications, experimental data were reported which prove that melts simultaneously contain differently coordinated structural units. For instance, an X-ray absorption fine structure (XAFS) study (Okamoto et al., 2002b) of molten LaCl₃ led the authors to conclude that the melt contains (LaCl₆)^{3–}, (LaCl₇)^{4–}, and (LaCl₈)^{5–}. Studies of NdCl₃ and DyCl₃ melts by the same method were, however, less informative because of instrumental limitations (Matsuura et al., 2001). The presence of diverse structural forms follows from the data on ScCl₃–CsCl binary mixture melts. The Raman spectra of these melts showed the presence of not only (ScCl₆)^{3–} but also (ScCl₇)^{4–} with the CN of Sc³⁺ equal to 7 (Zissi and Papatheodorou, 2002). Interestingly, the $v_{\rm I}(A_{1g})$ vibrational frequency of (ScCl₆)^{3–} is higher than that of (ScCl₇)^{4–} by approximately 6%. A similar decrease by 6% is observed for the $v_{\rm I}(A_{1g})$ frequency of molten yttrium trichloride compared with lanthanide trichloride melts in the subgroup La–Sm (see Figure 21).

The appearance in melts of structures with higher CNs should undoubtedly cause a jump increase in heat capacity because of the increase in the number of vibrations. The structure of melts is likely indeed complex and contains separate structural units with different cation CNs. This is difficult to prove on the basis of Raman spectra because of the closeness of vibrational frequencies and low spectral resolution. The $v_l(A_{1g})$ frequency observed for ScCl₃–CsCl mixtures (Zissi and Papatheodorou, 2002) (see above) is actually an example of successful recording under the conditions of a low doublet resolution. The high- and low-frequency shoulders were assigned to different structural units thanks to noticeable changes in their concentrations as experimental conditions were varied.

According to Figure 21, we should not expect noticeable changes in the ratio between different structural units in melts of lanthanide trihalides that have identical structures in the solid state. A noticeable change in this ratio is likely characteristic of melts of lanthanide trichlorides only in going from hexagonal to monoclinic structures.

The recommended heat capacities of liquid RF₃ and RCl₃ were estimated from their experimental values (Dworkin and Bredig, 1963a,b, 1971; Gaune-Escard et al., 1994; Lyapunov et al., 2000a,b, 2004; Rycerz and Gaune-Escard, 2002a,b,c; Savin and Mikhailova, 1981; Savin et al., 1979; Spedding and Henderson, 1971; Spedding et al., 1974). We also



FIGURE 22 Dependences of $C_p^{\circ}(\text{RCl}_3,\text{liq})$ and C_{lat}° on the inverse ionic radius for six-coordinate \mathbb{R}^{3+} : \bigtriangledown , data from Dworkin and Bredig (1963a); \blacktriangle , data from Dworkin and Bredig (1963b); \diamondsuit , data from Dworkin and Bredig (1971); \blacksquare , data from Gaune-Escard et al. (1994) and Rycerz and Gaune-Escard (2002a,b,c); solid line, our calculation of C_{lat}° ; and \bigcirc , recommended data for $C_p^{\circ}(\text{RCl}_3,\text{liq})$ based on the results of this work.

considered the data from Pankratz (1984) (see Tables 25 and 26; Figures 22 and 23). The dependence of the $C_{lat}^{\circ}(liq) = C_{p}^{\circ}(liq) - C_{exs}^{\circ}(T_{m})$ difference on the inverse radius of R^{3+} cations was processed analytically to obtain correspondence with two criteria. Our task was to reproduce the linear dependences of $C_{lat}^{\circ}(liq)$ on the inverse ionic radius similar to those shown in Figure 21, but with the distinction that the lower the corresponding $v_l(A_{1g})$ frequency, the higher the $C_{lat}^{\circ}(liq)$ value as well as to minimize deviations of $C_{p}^{\circ}(liq)$ estimates from the experimental data.

The resulting values are listed in Tables 25 and 26. Note that the approximation was constructed without including data on LaCl₃ and PrCl₃ (Savin et al., 1979), CeCl₃ and NdCl₃ (Savin and Mikhailova, 1981), and LaF₃ (Spedding and Henderson, 1971). For comparison, Tables 25 and 26 also contain the results obtained by Kovács and Konings (2003), who analyzed the heat capacities of liquid lanthanide trifluorides and trichlorides with the assumption that heat capacity changes can be correlated with changes in $\Delta V/V$.

The selected procedure for estimating heat capacities gave a relative deviation of recommended values from the experimental data on 10 of a



FIGURE 23 Dependences of $C_p^{\circ}(RF_3, liq)$ and C_{lat}° on the inverse ionic radius of sixcoordinate R^{3+} : $\mathbf{\nabla}$, data from Spedding and Henderson (1971); $\mathbf{\Delta}$, data from Spedding et al. (1974); $\mathbf{\diamond}$, data from Lyapunov et al. (2000a,b, 2004); solid line, our calculation of C_{lat}° ; and \bigcirc , recommended data for $C_p^{\circ}(RF_3, liq)$ based on the results of this work.

total of 17 compounds that did not exceed the 3% instrumental error on heat capacity determinations. For three other compounds, the deviation was smaller than 4%. For the last four experimental data on LaCl₃ (Dworkin and Bredig, 1963b), $PrCl_3$ (Dworkin and Bredig, 1963a; Gaune-Escard et al., 1996), and DyCl₃ (Gaune-Escard et al., 1996), the relative deviations were larger and reached 10.7%, 8.8%, 5.8%, and 10.1%, respectively. Note that the relative deviation of the experimental heat capacity of TbCl₃ (Dworkin and Bredig, 1971) from our estimate is also within the instrumental error (1.4%), although its structure is different (orthorhombic in the crystalline state).

The agreement was much worse for lanthanide trifluorides. Of a total of 16 experimental values considered, only those for four compounds, SmF_3 (Spedding et al., 1974), DyF_3 (Lyapunov et al., 2000b), HoF_3 (Lyapunov et al., 2000a), and YbF₃ (Spedding et al., 1974), led to relative deviations comparable to measurement errors. For the other 12 compounds, deviations were larger, between 7–9% for five compounds and in the range 12–16% for five others. For two compounds, CeF₃ (Spedding et al., 1974) and HoF₃ (Spedding and Henderson, 1971), the deviations were quite large, 19% and 28%, respectively.

5.6 Thermodynamic functions

Our analytic description of the temperature dependence of heat capacities over the temperature range 298.15– $T_{\rm m}$ (in certain instances, over the temperature ranges 298.15– $T_{\rm tr}$ and $T_{\rm tr}$ – $T_{\rm m}$ separately) and the heat capacities in the liquid state at the temperatures of melting as well as of the enthalpies of phase transitions (including the temperatures of these transitions) can be used to calculate the thermodynamic functions of the compounds under consideration. The calculations were performed according to the procedure described in the previous section, and the resulting functions are listed in Table A6 in the form of the f_i coefficients (see Appendix).

Among lanthanide trichlorides, TbCl₃, DyCl₃, and ErCl₃ were reliably shown to experience polymorphic transitions. The heat capacities of the α polymorphs in the region of their existence were selected as follows.

The thermodynamic functions of TbCl₃ over the temperature range 783–855 K were calculated taking into account the heat capacities of the α polymorph (Dworkin and Bredig, 1971); these data described the heat capacity jump more realistically than those from Rycerz and Gaune-Escard (2002a). In the case of dysprosium and erbium trichlorides, their α polymorphs exist over narrow temperature ranges only and the enthalpies of the $\alpha \rightarrow \beta$ phase transitions are small. For this reason, we only considered the enthalpies of these transitions, as with lanthanide trifluorides (Chervonnyi and Chervonnaya, 2007a), and did not introduce jump changes in the heat capacities for the α polymorphs.

In the next section, we shall discuss the use of thermodynamic functions in calculations of heterogeneous equilibria involving lanthanide trichlorides. The results obtained will be analyzed to draw conclusions on the possibility of using the data described in this work for thermodynamic modeling purposes.

6. STANDARD THERMODYNAMIC PROPERTIES OF LANTHANIDE TRICHLORIDES

Systematized data on the enthalpies of sublimation at standard temperature of most of the lanthanide trichlorides can be found in two reviews, one written by Myers and Graves (1977b) and the other by Kovács and Konings (2003). In the first review, data on PmCl₃, SmCl₃, EuCl₃, and YbCl₃ are absent, while the second review does not contain data on PmCl₃ and SmCl₃. Published with a time gap of 26 years, these works contain data which, to within the specified uncertainties, agree for LaCl₃, CeCl₃, PrCl₃, and NdCl₃ and sharply differ starting with GdCl₃. Over the series GdCl₃–LuCl₃, the difference between the $\Delta_{sub}H^{\circ}$ (298) values for the same compound varies from ~ 6 to ~ 45 kJ/mol. The enthalpies of sublimation of all compounds given in Kovács and Konings (2003) are lower than those reported in Myers and Graves (1977b).

It might be thought that such discrepancies could be caused by the use by Myers and Graves (1977b) of much less experimental data on saturated vapor pressures and approximate estimates of the thermodynamic functions in the condensed state. However, recall that we introduced (Chervonnyi and Chervonnaya, 2004g) fairly large corrections into the thermodynamic functions of the gaseous state from Myers and Graves (1977a) used in the calculations performed by Myers and Graves (1977b). Later, we have casted well-founded doubts on the reliability of the initial thermophysical parameters selected by Kovács and Konings (2003) for calculating the thermodynamic functions of the condensed state (Chervonnyi and Chervonnaya, 2007b). Indeed, the reduced Gibbs energies were, as a rule, underestimated by Myers and Graves (1977a) by 5– 6 J/(mol·K), and strongly overestimated S° (298) values were recommended by Kovács and Konings (2003) for the crystalline state of several lanthanide trichlorides.

It follows that there was every reason to undertake a new systematic analysis of the enthalpies of sublimation of lanthanide trichlorides with the purpose of solving two problems. First, we aimed at revising the $\Delta_{sub}H^{\circ}(298)$ values for the whole series of compounds under consideration, including those for which data are absent in the two cited reviews (Kovács and Konings, 2003; Myers and Graves, 1977b). Second, and this was the main point, our purpose was to analyze the consistency of the $\Delta_{\rm sub}H^{\circ}(298, \text{III law})$ and $\overline{\Delta_{\rm sub}H^{\circ}(298, \text{II law})}$ enthalpies and the closeness of these values found from saturated vapor pressures over solid and liquid samples. We also wished to estimate the applicability of the thermodynamic functions of the gaseous (Chervonnyi and Chervonnava, 2004g) and condensed (Chervonnyi and Chervonnaya, 2007b) states to calculations of equilibria. Here and throughout, $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{\text{sub}}H^{\circ}(298, \text{ II law})$ denote the enthalpies of sublimation under standard conditions calculated according to the third and second laws of thermodynamics.

An additional proof of the validity of the solutions we propose for these problems can be obtained by comparing the data on sublimation (vaporization) of pure compounds with the data on the equilibrium constants (Chervonnyi, 1975, 1977b) of gas-phase reactions in the R + MCl₂ systems (M = Ba, Eu) and the appearance energies, AE (R⁺/RCl₃) (Evdokimov et al., 1984; Sapegin, 1984; Sapegin et al., 1984). This can conveniently be done by comparing a unique parameter for the compounds under study. Recently, we considered this possibility in the case of lanthanum (Chervonnyi and Chervonnaya, 2004b), samarium (Chervonnyi and Chervonnaya, 2004e), europium (Chervonnyi and Chervonnaya, 2004a, 2005b), and ytterbium (Chervonnyi and Chervonnaya, 2004f) chlorides by analyzing the convergence of the enthalpies of atomization $\Delta_{at}H^{\circ}(298)$. However, note that calculations of reliable $\Delta_{at}H^{\circ}(298)$ values from $\Delta_{sub}H^{\circ}(298)$ require verified data on the enthalpies of formation of crystalline lanthanide trichlorides $\Delta_{f}H^{\circ}$ (RCl₃, cr, 298). We therefore had to perform an additional refining analysis of the corresponding values recommended by Cordfunke and Konings (2001a).

6.1 Enthalpies of formation of crystalline compounds

Sytematic determinations of the experimental enthalpies of formation of lanthanide trichlorides have been performed repeatedly (Bratsch and Silber, 1982; Cordfunke and Konings, 2001a; Hisham and Benson, 1987; Laptev, 1996; Morss, 1994; Struck and Baglio, 1992). The last work in this series propose a selection of the most reliable $\Delta_f H^\circ$ (RCl₃, cr, 298) values among the experimental data available reported by Cordfunke and Konings (2001a). As follows from Table 27, the values recommended these authors differ from the earlier estimates (Barin, 1995). In certain instances, discrepancies are as large as 10 kJ/mol.

During long-term studies of the properties of the compounds under consideration (starting in the 1950s), efforts have been made to reveal tendencies in $\Delta_{\rm f} H^{\circ}({\rm RCl}_3, {\rm cr}, 298)$ variations to obtain reliable estimates of the lacking data (in the first place, those of PmCl₃). As follows from Cordfunke and Konings (2001a), the most reliable estimates can be obtained using Morss' method (1994). Its essence is as follows.

The heat of formation of ions in an aqueous medium is determined using the reaction

$$\operatorname{RCl}_3(\operatorname{cr}) = \operatorname{R}^{3+}(\operatorname{aq}) + \operatorname{3Cl}^-(\operatorname{aq})$$

as

$$\Delta_{\rm f} H^{\circ}({\rm R}^{3+},{\rm aq},298) = \Delta_{\rm r} H^{\circ}(298) + \Delta_{\rm f} H^{\circ}({\rm RCl}_3,{\rm cr},298) - 3\Delta_{\rm f} H^{\circ}({\rm Cl}^-,{\rm aq},298),$$

that is, through the heat of solution of RCl₃ $\Delta_r H^{\circ}(298)$, the heat of formation of crystalline RCl₃, and the enthalpy of formation of the Cl⁻ ion in an aqueous medium. Morss (1994) noted that the difference in the enthalpies of formation [$\Delta_f H^{\circ}(\text{RCl}_3, \text{ cr}, 298) - \Delta_f H^{\circ}(\text{R}^{3+}, \text{ aq}, 298)$] is determined by the enthalpy of solution (that is by the enthalpy of the reaction given above) which, in turn, depends on the crystal lattice parameters of RCl₃. Cordfunke and Konings (2001a) used the crystal-chemical radii of R³⁺ cations with the CN equal to 6 as a characteristic structural parameter.

R	R ³⁺ , aq ^a	RCl ₃ , cr ^b	RCl ₃ , cr ^c	RCl ₃ , cr ^d	δ[Δ _f H° (298)]
La	-707.6 ± 2.5	-1071.1	-1071.6 ± 1.5	-1071.6 ± 1.5	0
Ce	-702.4 ± 2.0	-1053.5	-1059.7 ± 1.5	-1060.1 ± 1.5	0.4
Pr	-705.7 ± 2.0	-1056.9	-1058.6 ± 1.5	-1057.5 ± 1.5	-1.1
Nd	-694.8 ± 2.0	-1041.8	-1040.9 ± 1.0	-1041.1 ± 1.0	0.2
Pm	-693 ± 10	-	-1030 ± 10	-1033.7 ± 10	3.7
Sm	-690.0 ± 2.0	-1025.9	-1025.3 ± 2.0	-1025.3 ± 2.0	0
Eu	-605.4 ± 4.0	-936.0	-935.4 ± 3.0	-935.4 ± 3.0	0
Gd	-698.4 ± 2.0	-1008.0	-1018.2 ± 1.5	-1023.3 ± 1.5	5.1
Tb	-699.8 ± 4.0	-997.0	-1010.6 ± 3.0	-1010.6 ± 3.0	0
Dy	-700.2 ± 3.0	-989.9	-993.1 ± 3.0	-992.4 ± 3.0	-0.7
Ho	-707.7 ± 3.0	-1005.4	-997.7 ± 2.5	-997.5 ± 2.5	-0.2
Er	-708.2 ± 3.0	-994.5	-994.4 ± 2.0	-995.5 ± 2.0	1.1
Tm	-711.1 ± 3.0	-986.6	-996.3 ± 2.5	-996.2 ± 2.5	-0.1
Yb	-676.3 ± 3.0	-959.8	-959.5 ± 3.0	-959.2 ± 3.0	-0.3
Lu	-703.3 ± 3.0	_	-987.1 ± 2.5	-984.2 ± 2.5	-2.9

TABLE 27 Enthalpies of formation $\Delta_{f}H^{\circ}(RCl_{3}, cr, 298)$ and $\Delta_{f}H^{\circ}(R^{3+}, ag, 298)$, kJ/mol

^a Cordfunke and Konings (2001b).

^b Barin (1995).
^c Cordfunke and Konings (2001a).

^d Our calculations.

In spite of different types of crystal lattices in the series of lanthanide trichlorides, the approach used by Cordfunke and Konings (2001a) was justified. This follows from the data obtained by Shannon (1976), according to which the dependences of ionic radii on R^{3+} yield parallel curves alone the lanthanide series when different CNs are considered. This method is the most attractive, since it involves a systematic selection (Cordfunke and Konings, 2001b) of the enthalpies of formation $\Delta_{f}H^{\circ}$ (R³⁺, aq, 298). Our repeat analysis of the enthalpies of formation of lanthanide trichlorides, however, showed that introduction of some corrections into their values was necessary.

We reproduced the dependence of the differences [$\Delta_{f}H^{\circ}(RCl_{3}, cr, 298)$] $-\Delta_{\rm f} H^{\circ}(\dot{\rm R}^{3+}, {\rm aq}, 298)]$, taken from Cordfunke and Konings (2001a), on the crystal-chemical radii of R^{3+} for a CN of 6, however, using the ionic radii (Shannon, 1976) described by a polynomial of degree 2. This polynomial had the form

 $r = 1.04792 - 0.01628n + 2.45155 \times 10^{-4}n^{2}$

where n = 1-15 in the series $La^{3+}-Lu^{3+}$.

The necessity of using smoothed values was discussed by us when selecting the enthalpies of formation of crystalline lanthanide dichlorides (Chervonnyi and Chervonnaya, 2005c).

With smoothed crystal-chemical radii (see Figure 24), $\delta[\Delta_f H^\circ$ (298)] = [$\Delta_f H^\circ$ (RCl₃, cr, 298) – $\Delta_f H^\circ$ (R³⁺, aq, 298)] values more accurately fall on two straight lines compared with data from Cordfunke and Konings (2001a).

When the enthalpies of formation of lanthanide trichlorides lying on these two straight lines were calculated, it was found that the difference between the $\delta[\Delta_f H^{\circ}(298)]$ values and the data from Cordfunke and Konings (2001a) was 0.1–1.1 kJ/mol (Table 27). We believe that Figure 24 more accurately describes the dependence of this parameter on crystal-chemical radii of R³⁺ for lanthanide trichlorides, which requires the introduction of several corrections into the results published by Cordfunke and Konings (2001a). First, the enthalpy of formation of PmCl₃ should be revised (-1033.7 ± 10 kJ/mol). Next, a more reliable $\Delta_f H^{\circ}$ (LuCl₃, cr, 298) value should be recommended, -984.2 ± 2.5 kJ/ mol; this value virtually coincides with that obtained by Merli et al. (1998) (-984.9 ± 2.5 kJ/mol). Lastly, the result for GdCl₃ must be amended. Instead of -1018.2 ± 1.5 kJ/mol, the -1023.3 ± 1.5 kJ/mol



FIGURE 24 Dependence of the difference of the enthalpies of formation $\delta[\Delta_{f}H^{\circ}(298)] = [\Delta_{f}H^{\circ}(RCl_{3}, cr, 298) - \Delta_{f}H^{\circ}(R^{3+}, aq, 298)]$ on crystal-chemical radii of R^{3+} ions; \bigcirc , according to Cordfunke and Konings (2001a); and \blacksquare , corrected data (Chervonnyi and Chervonnaya, 2007g). Reproduced from Chervonnyi and Chervonnaya (2007g) with permission from Pleiades Publishing, Ltd.

value should be used because $GdCl_3$ has the same crystal lattice as all the lanthanide trichlorides from lanthanum to europium.

The construction of similar dependences for RBr_3 and RI_3 according to the data reported by Cordfunke and Konings (2001a) and for R_2O_3 using data from the same authors (Cordfunke and Konings, 2001c) and/or published in IVTANTERMO (2004) also allows the presence of different crystal lattices within a series of compounds of the same type to be identified more clearly.

6.2 Calculations of sublimation enthalpies

The enthalpies of sublimation under standard conditions were calculated by the second and third laws of thermodynamics from the experimental saturated vapor pressures (Block and Campbell, 1961; Brewer, 1950; Brunetti et al., 1999, 2000, 2003, 2004; Chervonnyi and Chervonnaya, 2004a,b,e,f, 2005b; Chervonnyi et al., 1973, 1974; Dudchik et al., 1969a,b; Evseeva and Zenkevich, 1976, 1978, 1979; Hannay and Myers, 1979; Harrison, 1952; Hastie et al., 1968; Kapala et al., 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003b; Kudin and Vorob'ev, 2003; Kudin et al., 1993b, 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a,b, 1999; Moriarty, 1963; Myers and Hannay, 1980; Nesmeyanov and Sazonov, 1959; Nisel'son et al., 1978; Novikov and Baev, 1962a,b, 1964; Novikov and Gavryuchenko, 1965a,b; Pashinkin et al., 1962; Piacente et al., 2002, 2003; Pogrebnoi et al., 1997, 2001; Polyachenok, 1972; Scardala et al., 2003; Shimazaki and Niwa, 1962; Villani et al., 2000a,b, 2002) with the use of the thermodynamic functions described in Sections 2 and 5. The data obtained are summarized in Tables 28–41. In calculations according to the second law, $\Delta_{sub}H^{\circ}(T)$ values were determined from the slopes of semilogarithmic plots; the *T* value was set equal to the mean temperature of measurements.

It follows from Tables 28–41 that the convergence of the $\Delta_{sub}H^{\circ}(298, III law)$ and $\Delta_{sub}H^{\circ}(298, II law)$ values obtained in our calculations is quite satisfactory. A total of 114 saturated vapor pressure measurements were performed for 14 of the 15 lanthanide trichlorides (all except PmCl₃). These values were used to calculate the enthalpies of sublimation by the second and third laws of thermodynamics simultaneously. Of these 114 results, 39 were obtained for vapor pressures over solids and 75 for vapor pressures over liquid samples.

Calculations from the data on the sublimation of lanthanide trichlorides gave differences between $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{sub}H^{\circ}(298, \text{II law})$ smaller than 2 kJ/mol in four instances, for LaCl₃ (Kudin and Vorob'ev, 2003; Kudin et al., 2003b) and TmCl₃ (Khasanshin et al., 2001a; Kudin et al., 2000); differences of 2–3 kJ/mol in six instances, for CeCl₃ (Kapala et al., 2002; Villani et al., 2000a), NdCl₃ (Kudin and Vorob'ev, 2003; Villani

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298	, III law)	
αα	liq ^b	α ^a	liq ^b	References
_	_	333.8 <i>,</i> 335.4	334.8	Harrison (1952)
311.9	-	331.9	_	Nesmeyanov and Sazonov (1959)
_	-	_	337.5	Block and Campbell (1961)
324.3	-	344.7	_	Shimazaki and Niwa (1962)
-	-	-	325.6, 324.1, 319.0	Moriarty (1963)
_	404.5	_	344.5	Novikov and Baev (1962a)
_	410.3	_	342.6	Novikov and Baev (1962b)
_	335.7	_	341.0	Novikov and Baev (1964)
330.6	-	_	_	Hastie et al. (1968)
_	342.6	_	341.2	Dudchik et al. (1969a)
_	342.9	_	341.8	Polyachenok (1972)
_	381.5	_	343.2	Nisel'son et al. (1978)
348.0	350.4	340.3	339.6	Brunetti et al. (2000)
338.1	-	339.0	_	Kudin and Vorob'ev (2003)
338.4	-	339.2	_	Kudin et al. (2003b)
-	340.1	-	340.4	Chervonnyi and Chervonnaya (2004b)

TABLE 28 Enthalpies of sublimation for LaCl₃ (kJ/mol)

^{*a*} Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

et al., 2002), EuCl₃ (Chervonnyi and Chervonnaya, 2004b, 2005b), and TmCl₃ (Brunetti et al., 2004); discrepancies of 3–5 kJ/mol in five instances, for CeCl₃ (Kudin and Vorob'ev, 2003), PrCl₃ (Kudin et al., 2003a; Shimazaki and Niwa, 1962), ErCl₃ (Kudin and Vorob'ev, 2003), and YbCl₃ (Chervonnyi and Chervonnaya, 2004f); and discrepancies of 5–9 kJ/mol in nine instances, for LaCl₃ (Brunetti et al., 2000), PrCl₃ (Kapala et al., 2002; Villani et al., 2000b), NdCl₃ (Kudin and Smirnov, 2003b), HoCl₃ (Kudin et al., 1997b), ErCl₃ (Brunetti et al., 2003), TmCl₃ (Kudin and Vorob'ev, 2003), and LuCl₃ (Kudin and Vorob'ev, 2003; Pogrebnoi et al., 1997). For the other 15 measurements, for LaCl₃ (Nesmeyanov and Sazonov, 1959; Shimazaki and Niwa, 1962), CeCl₃ (Pogrebnoi et al., 2001; Shimazaki and Niwa, 1962), NdCl₃ (Kapala et al., 2002), SmCl₃ (Pashinkin et al., 1997a), HoCl₃ (Kudin and Vorob'ev, 2003;

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298,	III law)			
αα	liq ^b	αα	liq ^b	References		
-	-	329.0, 330.1	327.8	Harrison (1952)		
-	-	_	333.3	Block and Campbell (1961)		
316.1	_	335.6	_	Shimazaki and Niwa (1962)		
-	-	_	324.1, 327.3, 327.2, 328.9	Moriarty (1963)		
-	356.8	_	336.9	Novikov and Baev (1962a)		
-	383.0	_	335.0	Novikov and Baev (1962b)		
-	325.3	_	333.1	Novikov and Baev (1964)		
-	340.7	_	333.1	Dudchik et al. (1969a)		
-	338.4	_	333.2	Polyachenok (1972)		
334.5	-	331.9	_	Villani et al. (2000a)		
323.0	-	336.3	_	Pogrebnoi et al. (2001)		
327.3	-	329.7	_	Kapala et al. (2002)		
323.0	_	326.8	_	Kudin and Vorob'ev (2003)		

TABLE 29 Enthalpies of sublimation for CeCl₃ (kJ/mol)

 a Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

Kuznetsov et al., 1999; Piacente et al., 2002), YbCl₃ (Kudin and Vorob'ev, 2003; Kudin et al., 1997a,b; Kuznetsov et al., 1997b), and LuCl₃ (Kudin et al., 1997b; Pogrebnoi et al., 1997), differences between the $\Delta_{sub}H^{\circ}$ (298, III law) and $\Delta_{sub}H^{\circ}$ (298, II law) values were within the interval 9.7–55.6 kJ/mol.

For vaporization studies, a difference smaller than 2 kJ/mol was observed in nine instances, for LaCl₃ (Chervonnyi and Chervonnaya, 2004b; Dudchik et al., 1969a; Polyachenok, 1972), PrCl₃ (Novikov and Baev, 1964), NdCl₃ (Nisel'son et al., 1978), GdCl₃ (Polyachenok, 1972), TbCl₃ (Myers and Hannay, 1980), DyCl₃ (Myers and Hannay, 1980), and ErCl₃ (Novikov and Gavryuchenko, 1965a,b); a difference between 2 and 3 kJ/mol occurs for PrCl₃ (Kudin et al., 2003a), while differences between 3 and 5 kJ/mol are detected in seven instances, for PrCl₃ (Polyachenok, 1972), NdCl₃ (Kudin and Vorob'ev, 2003), GdCl₃ (Dudchik et al., 1969b;

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298,	III law)			
αα	liq ^b	α ^α	liq ^b	References		
_	-	322.5 <i>,</i> 323.6	320.6	Harrison (1952)		
_	_	_	330.5	Block and Campbell (1961)		
316.0	-	312.7	_	Shimazaki and Niwa (1962)		
-	-	_	319.5, 324.7, 327.2, 326.8	Moriarty (1963)		
-	362.7	_	331.4	Novikov and Baev (1962a)		
-	284.3	_	321.6	Novikov and Baev (1962b)		
_	330.8	_	329.1	Novikov and Baev (1964)		
_	329.3	_	325.2	Polyachenok (1972)		
_	383.7	_	338.5	Nisel'son et al. (1978)		
-	325.7	_	332.3	Hannay and Myers (1979)		
336.3	333.2	329.3	327.8	Villani et al. (2000b)		
331.8	278.5	326.7	327.6	Kapala et al. (2002)		
320.2	320.7	324.8	318.1	Kudin et al. (2003a)		

TABLE 30 Enthalpies of sublimation for PrCl₃ (kJ/mol)

 a Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

Khasanshin et al., 2001b; Piacente et al., 2003), SmCl₃ (Polyachenok, 1972), and LuCl₃ (Nisel'son et al., 1978; Polyachenok, 1972). Larger differences, namely between 5 and 9 kJ/mol, appear in 19 instances, for LaCl₃ (Novikov and Baev, 1964), PrCl₃ (Hannay and Myers, 1979; Villani et al., 2000b), CeCl₃ (Dudchik et al., 1969a; Novikov and Baev, 1964; Polyachenok, 1972), NdCl₃ (Dudchik et al., 1969a; Novikov and Baev, Polyachenok, SmCl₃ 1962a,b, 1964; 1972), (Chervonnyi and Chervonnaya, 2004e; Kudin and Vorob'ev, 2003; Pogrebnoi et al., 2001), EuCl₃ (Polyachenok, 1972), GdCl₃ (Kudin and Vorob'ev, 2003), DyCl₃ (Brunetti et al., 1999; Kapala et al., 2002), HoCl₃ (Piacente et al., 2002), and ErCl₃ (Dudchik et al., 1969a; Polyachenok, 1972). Differences between 9 and 20 kJ/mol are detected in 22 instances, for LaCl₃ (Brunetti et al., 2000), CeCl₃ (Novikov and Baev, 1962a), NdCl₃ (Evseeva and Zenkevich, 1976; Kapala et al., 2002; Kudin and Smirnov, 2003b; Shimazaki and Niwa, 1962; Villani et al., 2002), SmCl₃ (Chervonnyi et al., 1974), GdCl₃

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298	3, III law)	
αα	liq ^b	αα	liq ^b	References
_	_	314.3 <i>,</i> 315.4	311.9	Harrison (1952)
-	-	-	326.3	Block and Campbell (1961)
-	309.4	-	328.0	Shimazaki and Niwa (1962)
-		-	321.0, 319.5, 327.1, 331.0, 328.1	Moriarty (1963)
-	333.4	-	326.5	Novikov and Baev (1962a,b, 1964)
-	322.6	_	327.7	Dudchik et al. (1969a)
-	321.4	-	327.9	Polyachenok (1972)
-	331.3	-	320.7	Evseeva and Zenkevich (1976)
-	331.7	_	331.9	Nisel'son et al. (1978)
-	440.1	_	376.1	Kudin et al. (1993b)
328.9	344.1	326.8	329.9	Villani et al. (2002)
300.6	314.6	324.2	325.9	Kapala et al. (2002)
311.0	313.8	313.2	309.7	Kudin and Vorob'ev (2003)
318.7	300.1	313.6	309.4	Kudin and Smirnov (2003b)

 TABLE 31
 Enthalpies of sublimation for NdCl₃ (kJ/mol)

^{*a*} Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

(Myers and Hannay, 1980), TbCl₃ (Dudchik et al., 1969b; Piacente et al., 2003; Polyachenok, 1972), DyCl₃ (Kuznetsov et al., 1997a; Polyachenok, 1972), HoCl₃ (Dudchik et al., 1969a; Kudin et al., 1997b; Polyachenok, 1972), TmCl₃ (Dudchik et al., 1969a; Polyachenok, 1972), YbCl₃ (Polyachenok, 1972), and LuCl₃ (Dudchik et al., 1969a; Polyachenok, 1972). Lastly, 17 difference values between $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{sub}H^{\circ}(298, \text{III law})$ were within the interval 24.6–67.7 kJ/mol for LaCl₃ (Nisel'son et al., 1978; Novikov and Baev, 1962a,b), CeCl₃ (Novikov and Baev, 1962b), PrCl₃ (Kapala et al., 2002; Nisel'son et al., 1978; Novikov and Baev, 1962a,b), NdCl₃ (Kudin et al., 1993b), SmCl₃ (Scardala et al., 2003), GdCl₃ (Evseeva and Zenkevich, 1978), TbCl₃ (Kuznetsov et al., 1999).

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298	3, III law)	
αα	liq ^b	α ^a	liq ^b	References
_	-	247.5, 256.8	267.4	Brewer (1950)
198.4	-	254.0	_	Pashinkin et al. (1962)
-	-	-	285.5, 289.6, 303.0, 314.9, 317.3	Moriarty (1963)
-	313.7	_	308.8	Polyachenok (1972)
-	294.7	_	_	Chervonnyi et al. (1973)
-	305.4	_	318.1	Chervonnyi et al. (1974)
-	300.2	_	306.5	Pogrebnoi et al. (2001)
302.8	289.6	315.0	318.8	Scardala et al. (2003)
_	300.2	-	306.5	Kudin and Vorob'ev (2003)
_	305.3	-	312.6	Chervonnyi and Chervonnaya (2004e)

TABLE 32 Enthalpies of sublimation for SmCl₃ (kJ/mol)

 $^a\,$ Calculated from saturated vapor pressures over the α phase. $^b\,$ Calculated from saturated vapor pressures over melts.

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(2	298, III law)	
αα	liq ^b	a^{b} α^{a} liq ^b		References
_	_	_	295.5	Block and Campbell (1961)
-	-	-	274.0, 277.7, 284.7, 299.5	Moriarty (1963)
-	307.5	-	299.9	Polyachenok (1972)
278.0		275.0		Chervonnyi and
				Chervonnaya (2004a,
				2005b)

TABLE 33 Enthalpies of sublimation for EuCl₃ (kJ/mol)

^{*a*} Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

It follows that the difference between $\Delta_{sub}H^{\circ}(298, III \text{ law})$ and $\Delta_{sub}H^o(298, \text{ II law})$ is fairly small, within 9 kJ/mol, for 24 of 39 sublimation measurements and for 36 of 75 vaporization measurements. The 24

⊿ _{sub} H°(298, II law)		\varDelta_{sub}	H°(298, III law)	
αα	liq ^b	α ^α	liq ^b	References
_	_	_	298.3, 304.1, 305.8, 307.6	Moriarty (1963)
_	311.1	_	315.2	Dudchik et al. (1969b)
_	316.3	_	315.5	Polyachenok (1972)
-	284.8	-	309.4	Evseeva and Zenkevich (1978)
_	326.0	_	315.5	Myers and Hannay (1980)
_	294.1	_	298.7	Khasanshin et al. (2001b)
_	317.8	_	313.5	Piacente et al. (2003)
-	292.7	-	300.6	Kudin and Vorob'ev (2003)

TABLE 34 Enthalpies of sublimation for GdCl₃ (kJ/mol)

^{*a*} Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

⊿ _{sub} H°(298, II law)		$\varDelta_{\sf sub} {\cal H}^{\circ}$ (298, III law)			
α^a liq ^b		α^a liq ^b		References	
_	-	-	299.2	Block and Campbell (1961)	
_	-	-	306.5, 303.5, 317.5, 317.7	Moriarty (1963)	
_	294.8	-	310.1	Dudchik et al. (1969b)	
_	294.2	_	310.2	Polyachenok (1972)	
_	307.5	_	308.3	Myers and Hannay (1980)	
_	291.6	_	316.2	Khasanshin et al. (1999)	
_	287.7	_	314.8	Kudin et al. (2000)	
_	290.9	_	302.7	Piacente et al. (2003)	
-	291.3	-	316.0	Kudin and Vorob'ev (2003)	

 TABLE 35
 Enthalpies of sublimation for TbCl₃ (kJ/mol)

 $^{\it a}\,$ Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

and 36 values selected include all lanthanide trichlorides studied. Note that some of the 60 (24 + 36) data for given trichlorides (LaCl₃, CeCl₃, PrCl₃, NdCl₃, HoCl₃, ErCl₃, and LuCl₃) include measurements of both sublimation and vaporization enthalpies. This allowed us to analyze the whole set of data presented in Tables 28–41 with the purpose of selecting the most reliable values.

⊿ _{sub} H°(298, II law)		$\varDelta_{\sf sub} {\cal H}^{\circ}$ (298, III law)		
αα	liq ^b	α ^α	liq ⁶	References
_	_	-	290.2	Block and Campbell (1961)
-	-	_	282.0, 285.4, 284.8, 287.8	Moriarty (1963)
_	276.7	-	302.8	Dudchik et al. (1969b)
_	287.0	-	302.9	Polyachenok (1972)
_	302.2	-	300.9	Myers and Hannay(1980)
_	251.4	_	294.5	Evseeva and Zenkevich (1979)
272.6	270.2	287.0	287.8	Kuznetsov et al. (1997a) and Kudin et al. (1997a,b)
-	289.9	-	297.7	Brunetti et al. (1999)
_	301.7	-	295.4	Kapala et al. (2002)
-	-	290.6	289.6	Kudin and Vorob'ev (2003) ^c

Enthalpies of sublimation for DyCl₃ (kJ/mol) TABLE 36

 ^a Calculated from saturated vapor pressures over the α phase.
 ^b Calculated from saturated vapor pressures over melts.
 ^c In this work, semilogarithmic plots over the temperature range 770–1009 K are given for DyCl₃; calculations by the second law were not performed because this interval covers saturated vapor pressures for both the sublimation of the α polymorph and vaporization of liquid dysprosium trichloride.

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298, III law)		
αα	liq ^b	αª	liq ^b	References
_	_	_	293.8	Block and Campbell (1961)
-	-	-	296.3, 298.2,	Moriarty (1963)
			295.2, 274.3	
-	291.1	-	303.4	Dudchik et al. (1969a)
-	289.2	-	304.4	Polyachenok (1972)
312.3	287.3	304.2	304.4	Kudin et al. (1997b)
271.7	231.4	303.8	296.8	Kuznetsov et al. (1999)
289.4	292.7	302.4	301.7	Piacente et al. (2002)
292.8	-	302.5	_	Kudin and Vorob'ev
				(2003)

TABLE 37 Enthalpies of sublimation for HoCl₃ (kJ/mol)

 a Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

⊿ _{sub} H°(298, II law)		${\it \Delta}_{{ m sub}}{\it H}^{\circ}$ (298, III law)			
αα	liq ^b	α ^α	liq ^b	References	
_	_	_	295.4	Block and Campbell (1961)	
-	-	-	290.8, 299.2, 312.0, 311.8	Moriarty (1963)	
-	301.3	-	302.4	Novikov and Gavryuchenko (1965a,b)	
_	293.3	-	301.7	Dudchik et al. (1969a)	
_	293.5	-	302.1	Polyachenok (1972)	
308.1	-	300.0	_	Brunetti et al. (2003)	
293.5	-	298.0	-	Kudin and Vorob'ev (2003)	

TABLE 38 Enthalpies of sublimation for ErCl₃ (kJ/mol)

^{*a*} Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298, III law)		
α ^a	liq ^b	α ^a	liq ^b	References
_	_	_	295.7	Block and Campbell (1961)
_	_	_	298.0, 292.4,	Moriarty (1963)
			300.6, 288.5	
-	284.7	-	302.8	Dudchik et al. (1969a)
-	288.0	-	302.5	Polyachenok (1972)
294.2	-	295.3	_	Kudin et al. (2000)
293.9	-	294.7	_	Khasanshin et al. (2001a)
288.9	-	294.3	_	Kudin and Vorob'ev (2003)
304.2	_	301.5	-	Brunetti et al. (2004)

TABLE 39 Enthalpies of sublimation for TmCl₃ (kJ/mol)

^{*a*} Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

6.2.1 Lanthanum trichloride

Among the 16 studies devoted to LaCl₃ (see Table 28), 5 measurements (Chervonnyi and Chervonnaya, 2004b; Dudchik et al., 1969a; Kudin and Vorob'ev, 2003; Kudin et al., 2003b; Polyachenok, 1972) gave coincidental values within ~1 kJ/mol when the enthalpies of sublimation were calculated by the second and third laws and within ~2 kJ/mol when the enthalpies of sublimation were calculated by the third law from the data of different works. We selected the mean value (340.3 \pm 3.0 kJ/mol) of these five results as the recommended value.

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298, III law)		
αα	liq ^b	α ^α	liq ^b	References
_	_	_	297.5	Block and Campbell (1961)
-	-	-	310.9, 311.5, 314.4, 316.6	Moriarty (1963)
-	285.0	-	303.8	Polyachenok (1972)
296.3	-	327.3	_	Kudin et al. (1997a,b) and Kuznetsov et al. (1997b)
296.3	-	327.8	_	Kudin and Vorob'ev (2003)
310.4	-	306.9	_	Chervonnyi and Chervonnaya (2004f)

TABLE 40 Enthalpies of sublimation for YbCl₃ (kJ/mol)

^{*a*} Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

⊿ _{sub} H°(298, II law)		⊿ _{sub} H°(298, III law)			
αα	liq ^b	α^a	liq ^b	References	
_	_	_	301.5	Block and Campbell (1961)	
-	_	303.0, 302.5	306.6	Moriarty (1963)	
-	291.6	_	301.6	Dudchik et al. (1969a)	
-	284.9	_	303.6	Polyachenok (1972)	
-	296.1	_	300.8	Nisel'son et al. (1978)	
279.4	_	305.8	-	Kudin et al. (1997b)	
283.9	_	292.6	-	Pogrebnoi et al. (1997) ^c	
279.0	_	305.2	-	Pogrebnoi et al. $(1997)^d$	
284.5	_	292.9	-	Kudin and Vorob'ev (2003)	

TABLE 41 Enthalpies of sublimation for LuCl₃ (kJ/mol)

^{*a*} Calculated from saturated vapor pressures over the α phase.

^b Calculated from saturated vapor pressures over melts.

^c From the absolute vapor pressures reported by Pogrebnoi et al. (1997).

^d From the analytic temperature dependence of vapor pressure according to Pogrebnoi et al. (1997).

6.2.2 Cerium trichloride

The 18 $\Delta_{sub}H^{\circ}(298, \text{III law})$ values calculated from the data of 13 studies (see Table 29) lie in the interval 324.1–336.9 kJ/mol. The mean value (331.1 kJ/mol) virtually coincides with those reported by Villani et al. (2000a) and Kapala et al. (2002), which, at the same time, were characterized by the $\Delta_{sub}H^{\circ}(298, \text{II law})$ values coinciding to within ~2 kJ/mol.

We therefore selected the above mean value (331.1 \pm 3.0 kJ/mol) as the recommended enthalpy of sublimation.

6.2.3 Praseodymium trichloride

The spread of $\Delta_{sub}H^{\circ}(298, \text{III law})$ values calculated from the data of 13 studies (see Table 30) is fairly large (312.7–338.5 kJ/mol). Among these data, the results obtained in vaporization studies by Novikov and Baev (1964) and Hannay and Myers (1979) as well as by calculations from saturated vapor pressure measured for the sublimation of PrCl₃ (Villani et al., 2000b), which were, in addition, characterized by a small difference between the $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{sub}H^{\circ}(298, \text{III law})$ values, could be singled out as being the most reliable. Therefore, their mean value (329.6 ± 3.0 kJ/mol) was selected as the recommended one.

6.2.4 Neodymium trichloride

The obviously incorrect result from Kudin et al. (1993b) could be ignored. The other 21 values for $\Delta_{sub}H^{\circ}(298, \text{III law})$ are characterized by a spread over the 309.7–331.9 kJ/mol interval (see Table 31). Close agreement between the results obtained using the third law (Nisel'son et al., 1978) and the data from Novikov and Baev (1962a,b, 1964) and Evseeva and Zenkevich (1976) calculated by the second law attracts attention. The recommended enthalpy of sublimation was therefore set to 331.8 ± 3.0 kJ/mol, value obtained from the measurements reported by Nisel'son et al. (1978). For these data, the difference between $\Delta_{sub}H^{\circ}$ (298, III law) and $\Delta_{sub}H^{\circ}(298, \text{ III law})$ was only 0.2 kJ/mol.

6.2.5 Promethium trichloride

The tendency observed for changes in the enthalpy of sublimation over the series LaCl₃-NdCl₃ allows us to recommend a value of 332 ± 3 kJ/mol as the enthalpy of sublimation of PmCl₃. We believe this value to be fairly reliable.

6.2.6 Samarium trichloride

The $\Delta_{sub}H^{\circ}(298, \text{III law})$ values are characterized by a fairly large spread (see Table 32). A pairwise comparison of the $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{sub}H^{\circ}(298, \text{III law})$ values showed that the enthalpy of sublimation found by the second law was, as a rule, smaller than that calculated by the third law. This was evidence of the occurrence of side decomposition reactions. An exception to this finding are calculations from the estimated temperature dependence of vapor pressure above the melting point (Polyachenok, 1972). The value 315.0 \pm 3.0 kJ/mol recommended by Chervonnyi and Chervonnaya (2004e) is the mean of the $\Delta_{sub}H^{\circ}$ (298, III law) values.

6.2.7 Europium trichloride

The recommended enthalpy of sublimation of EuCl₃ (275.0 \pm 3.0 kJ/mol) was selected on the basis of the $\Delta_{sub}H^{\circ}$ (298, III law) values (Chervonnyi and Chervonnaya, 2004a, 2005b) (see Table 33).

6.2.8 Gadolinium trichloride

All saturated vapor pressure measurements were performed over molten GdCl₃ (see Table 34). Among these results, some data could be singled out (Dudchik et al., 1969b; Myers and Hannay, 1980; Piacente et al., 2003; Polyachenok, 1972). Calculations of $\Delta_{sub}H^{\circ}(298$, III law) from these studies yielded results that differ by less than 2 kJ/mol. Although some results are consistent to within 0–0.3 kJ/mol between different studies (Dudchik et al., 1969b; Myers and Hannay, 1980; Polyachenok, 1972), they are sometimes characterized by a considerable spread of the $\Delta_{sub}H^{\circ}(298$, II, law) enthalpies toward both lower (Dudchik et al., 1969b) and higher (Myers and Hannay, 1980) values. The smallest difference between $\Delta_{sub}H^{\circ}(298$, III law) and $\Delta_{sub}H^{\circ}(298$, II law) was observed for the data from Piacente et al. (2003). The corresponding $\Delta_{sub}H^{\circ}(298$, III law) value was therefore selected as the recommended one (313.5 ± 3.0 kJ/mol).

6.2.9 Terbium trichloride

Calculations of $\Delta_{sub}H^{\circ}(298, \text{III law})$ from the saturated vapor pressures measured in nine studies (Block and Campbell, 1961; Dudchik et al., 1969b; Khasanshin et al., 2001b; Kudin and Vorob'ev, 2003; Kudin et al., 2000; Moriarty, 1963; Myers and Hannay, 1980; Piacente et al., 2003; Polyachenok, 1972) gave values spread over the interval 299.2–317.7 kJ/ mol (see Table 35) with a mean value of 310.2 kJ/mol. Almost all the $\Delta_{sub}H^{\circ}$ (298, II law) enthalpies were lower by \sim 10–20 kJ/mol than the corresponding $\Delta_{sub} H^{\circ}(298, \text{III law})$ values. There is, however, an exception, namely the result obtained from the data of Myers and Hannay (1980) for which the difference between $\Delta_{sub}H^{\circ}(298, III \text{ law})$ and $\Delta_{sub}H^{\circ}(298, II \text{ law})$ is as small as 0.8 kJ/mol. We consequently recommend this $\Delta_{sub}H^{\circ}$ (298, III law) value as the most reliable one (308.3 \pm 3.0 kJ/mol). It is slightly smaller than the mean value of all the results reported in the other studies (Block and Campbell, 1961; Dudchik et al., 1969b; Khasanshin et al., 2001b; Kudin and Vorob'ev, 2003; Kudin et al., 2000; Moriarty, 1963; Myers and Hannay, 1980; Piacente et al., 2003; Polyachenok, 1972).

6.2.10 Dysprosium trichloride

Close agreement between $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{sub}H^{\circ}(298, \text{II law})$ was only observed among the results of 3 of 11 studies (Brunetti et al., 1999; Kapala et al., 2002; Myers and Hannay, 1980) (see Table 36). Calculations from the data obtained by Myers and Hannay (1980) are

characterized by the smallest difference between these values. The $\Delta_{sub}H^{\circ}$ (298, III law) value found for vapor pressure measurements performed by these authors was therefore selected as the most reliable one (300.9 \pm 3.0 kJ/mol).

6.2.11 Holmium trichloride

The enthalpies of sublimation were calculated from saturated vapor pressure measurements performed in eight works (see Table 37). The $\Delta_{sub}H^{\circ}$ (298, III law) values calculated by processing data on both sublimation and vaporization (Dudchik et al., 1969a; Kudin and Vorob'ev, 2003; Kudin et al., 1997b; Piacente et al., 2002; Polyachenok, 1972) and, partly, from Kuznetsov et al. (1999) were consistent to within 2 kJ/mol. The corresponding $\Delta_{sub}H^{\circ}(298, \text{ II law})$ values were as a rule lower than $\Delta_{sub}H^{\circ}(298, \text{III law})$. There is, however, an exception. The data reported by Kudin et al. (1997b) and Kuznetsov et al. (1999) and obtained in one laboratory gave $\Delta_{sub}H^{\circ}(298, \text{ II law})$ enthalpies both above and below the corresponding $\Delta_{sub}H^{\circ}(298, \text{III law})$ values. The recommended enthalpy of sublimation of HoCl₃ (303.3 \pm 3.0 kJ/mol) was selected as the mean of the $\Delta_{sub}H^{\circ}(298, \text{III law})$ values calculated from eight values experimental data on vaporization (Dudchik et al., 1969a; Kudin et al., 1997b; Piacente et al., 2002; Polyachenok, 1972) and sublimation (Kudin and Vorob'ev, 2003; Kudin et al., 1997b; Kuznetsov et al., 1999).

6.2.12 Erbium trichloride

Among the data calculated from vapor pressure measurements over molten ErCl_3 (see Table 38), the $\Delta_{\text{sub}}H^\circ$ (298, III law) values obtained by processing the results of Dudchik et al. (1969a), Polyachenok (1972), and Novikov and Gavryuchenko (1965a,b) were within the interval 301.7– 302.4 kJ/mol. A fairly similar $\Delta_{\text{sub}}H^\circ$ (298, III law) value for solid terbium trichloride was obtained from the data of Kudin and Vorob'ev (2003) and Brunetti et al. (2003). The results found by Novikov and Gavryuchenko (1965a,b) are characterized by the closest agreement between the enthalpies of sublimation obtained according to the second and third laws of thermodynamics. We believe that the recommended enthalpy of sublimation of ErCl_3 can be determined from third law calculations on the basis of these data, namely 302.4 \pm 3.0 kJ/mol.

6.2.13 Thulium trichloride

The closest agreement between the $\Delta_{sub}H^{\circ}(298, \text{III law})$ values was obtained by processing the results from Dudchik et al. (1969a) and Polyachenok (1972) for vapor pressure determination and from Brunetti et al. (2004) for sublimation data (see Table 39). Note that the $\Delta_{sub}H^{\circ}$ (298, II law) value obtained from the data of Brunetti et al. (2004) is close to the $\Delta_{sub}H^{\circ}(298, \text{III law})$ enthalpies found in three other studies

(Brunetti et al., 2004; Dudchik et al., 1969a; Polyachenok, 1972). We selected the $\Delta_{sub}H^{\circ}(298, \text{III law})$ value calculated from the data of Brunetti et al. (2004) as the recommended one (301.5 ± 3.0 kJ/mol).

6.2.14 Ytterbium trichloride

The behavior of YbCl₃ at high temperatures is complicated by decomposition (Chervonnyi and Chervonnaya, 2004f). As a consequence, the enthalpies of sublimation of this compound calculated by the second and third laws of thermodynamics are characterized by a large spread (see Table 40). Chervonnyi and Chervonnaya (2004f) have analyzed the enthalpy of sublimation by averaging data previously published (Chervonnyi and Chervonnaya, 2004f; Moriarty, 1963; Polyachenok, 1972) together with an additional value ($\Delta_{sub}H^{\circ}(298) = 308.5 \pm 10 \text{ kJ/}$ mol) calculated from the appearance energy of the Yb⁺ ion formed in the ionization of the YbCl₃ molecule (Chervonnyi and Chervonnaya, 2004f). The resulted mean value corrected according to the refinement of the reduced Gibbs energy performed in this work gave $\Delta_{sub}H^{\circ}$ (298, III law) = 310.4 kJ/mol. In our view, this value is exaggerated, considering the recommended enthalpies of sublimation for the other lanthanide trichlorides. А more correct value is $\Delta_{\rm sub}H^{\circ}$ (298, II law) = 306. 9 \pm 3.0 kJ/mol obtained from saturated vapor pressure measurements (Chervonnyi and Chervonnaya, 2004f).

6.2.15 Lutetium trichloride

All the $\Delta_{sub}H^{\circ}(298, III \text{ law})$ values calculated from the measured saturated vapor pressures except, those presented in Kudin and Vorob'ev (2003) and Pogrebnoi et al. (1997), are within the interval 300.8–306.6 kJ/mol (see Table 41). Only one $\Delta_{sub}H^{\circ}(298, \text{ II law})$ value found by processing the data of Nisel'son et al. (1978) is in satisfactory agreement with them. We have noted some inconsistencies in some of the published results (Kudin and Vorob'ev, 2003; Kudin et al., 1997b; Pogrebnoi et al., 1997). The $\Delta_{sub}H^{\circ}(298, \text{III law})$ value found from the results reported by Kudin et al. (1997b) is 305.8 kJ/mol. The same authors presented two different sets of data (Pogrebnoi et al., 1997), namely, the results of saturated vapor pressure measurements and a semilogarithmic equation describing these measurements. Calculations from the data of the first kind yield $\Delta_{sub}H^{\circ}(298, \text{III law}) = 292.6$, and calculations based on the equation, 305.2 kJ/mol. Later on, Kudin and Vorob'ev (2003) reported a temperature dependence of vapor pressure from which $\Delta_{sub}H^{\circ}$ $(298, III law) = 292.9 \text{ kJ/mol could be extracted. Considering the recom$ mended values for the enthalpies of sublimation presented above for all the lanthanide trichlorides, we arrive at the conclusion that the enthalpy of sublimation of LuCl₃ found from the results obtained by Kudin et al. (1997b) is the most reliable (305.8 \pm 3.0 kJ/mol), although these measurements give a too low $\Delta_{sub}H^{\circ}(298$, II law) value.

6.3 Critical review of sublimation enthalpy values

During the whole period of studies on the vaporization and sublimation of lanthanide trichlorides, attempts have repeatedly been made to measure saturated vapor pressures for several compounds of the series under consideration. In the 1960s, systematic studies of these compounds were undertaken by Moriarty (1963) and the team headed by Novikov (Dudchik et al., 1969a,b; Novikov and Baev, 1962a,b, 1964; Novikov and Gavryuchenko, 1965a,b). Several experimental results presented by Polyachenok (1972) were also obtained with the participation of Novikov. More recently, after Myers and Graves (1977b) generalized the results obtained in studies of the vaporization of these compounds, values for the enthalpies of sublimation under standard conditions were recommended for virtually the whole series of lanthanide trichlorides, Myers and Hannay (Hannay and Myers, 1979; Myers and Hannay, 1980) performed new measurements of saturated vapor pressures over PrCl₃, GdCl₃, TbCl₃, and DyCl₃.

Several more recent studies should be mentioned. These are the most numerous results obtained by Kudin et al. in 1993–2003 (Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003b; Kudin and Vorob'ev, 2003; Kudin et al., 1993b, 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a,b, 1999; Pogrebnoi et al., 1997, 2001), which include experimental data on all the trichlorides except PmCl₃ and EuCl₃, and the data on CeCl₃, PrCl₃, NdCl₃, and DyCl₃ obtained by Kapala et al. (2002). Lastly, we must mention successive saturated vapor pressure measurements performed by Piacente et al. (Brunetti et al., 2000, 2003, 2004; Piacente et al., 2002, 2003; Scardala et al., 2003; Villani et al., 2000a,b, 2002) in 1999–2004. These authors have studied 11 of the 15 lanthanide trichlorides (PmCl₃, EuCl₃, YbCl₃, and LuCl₃ remain to be investigated).

The calculation results obtained by processing the data of Piacente et al. (Brunetti et al., 2000, 2003, 2004; Piacente et al., 2002, 2003; Scardala et al., 2003; Villani et al., 2000a,b, 2002) were selected for analyzing the reliability of the thermodynamic functions suggested for the compounds under consideration, especially for the compounds of the subseries DyCl₃–LuCl₃. There are several reasons for this selection. First, the data obtained by these authors are presented with experimental details, and measurements have been performed carefully. As a rule, several dozens of measurements were performed for one sample in a given temperature range and divided into separate series. Processing such data allows us to determine the spread of $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{sub}H^{\circ}(298, \text{II law})$ values in going from one sample to another. Next, these results are

characterized by the smallest deviations of $\Delta_{sub}H^{\circ}(298, III law)$ from the enthalpies of sublimation recommended by us among all the available systematic data. Indeed, the deviations from the values obtained by processing the corresponding data on vapor pressures over solids (sublimation studies) are, in kJ/mol, 0 for LaCl₃, 0.8 for CeCl₃, 0.3 for PrCl₃, 5.0 for NdCl₃, 0 for SmCl₃, 0.9 for HoCl₃, 2.4 for ErCl₃, and 0 for TmCl₃. Similarly, small deviations are found for calculations from the vapor pressures over liquids (vaporization studies): 0.7 for LaCl₃, 1.8 for PrCl₃, 1.9 for NdCl₃, 3.8 for SmCl₃, 0 for GdCl₃, 5.4 for TbCl₃, 3.2 for DyCl₃, and 1.6 for HoCl₃.

These statistical data are convincing evidence that the experimental results (Brunetti et al., 2000, 2003, 2004; Piacente et al., 2002, 2003; Scardala et al., 2003; Villani et al., 2000a,b, 2002) are highly reliable. The deviations of $\Delta_{sub}H^{\circ}(298$, II law) from $\Delta_{sub}H^{\circ}(298$, III law) and the recommended $\Delta_{sub}H^{\circ}(298)$ values can be used to draw conclusions about the quality of the thermodynamic functions themselves. We see that only one recommended enthalpy, the one for TbCl₃, is outside the interval of $\Delta_{sub}H^{\circ}$ (298, III law) values found from exerimental data. According to the results of these experimental studies, the $\Delta_{sub}H^{\circ}(298, III law)$ and $\Delta_{sub}H^{\circ}$ (298, III law) values do not overlap for 4 of a total of 11 compounds (LaCl₃, SmCl₃, TbCl₃, and HoCl₃). For the last three compounds (SmCl₃, TbCl₃, and HoCl₃), $\Delta_{sub}H^{\circ}(298, III law)$ is lower than $\Delta_{sub}H^{\circ}(298, III law)$.

On the whole, the relation between the $\Delta_{sub}H^{\circ}(298, \text{ II law})$ and $\Delta_{sub}H^{\circ}(298, \text{ III law})$ values observed suggests that the characteristic parameters (see Table 20) accepted for calculations of the temperature dependences of heat capacities do not need to be corrected. Indeed, a decrease in the Debye characteristic temperature and Einstein characteristic vibrational frequencies would increase $S^{\circ}(298)$ and, accordingly, reduce Gibbs energy values. Such corrections would decrease $\Delta_{sub}H^{\circ}(298, \text{ II law})$ enthalpies. This would improve the convergence between $\Delta_{sub}H^{\circ}$ (298, II law) and $\Delta_{sub}H^{\circ}(298, \text{ III law})$ for DyCl₃ and ErCl₃ but worsen the agreement between these values for TmCl₃ and YbCl₃ (Chervonnyi and Chervonnaya, 2004f).

Here, it is appropriate to show in a graphical form (see Figure 25) the different sets of recommended values for $\Delta_{sub}H^{\circ}(298)$, which stem from our analysis and from data reported by Myers and Graves (1977b) on one hand and by Kovács and Konings (2003) on the other hand. The substantial discrepancies between the results of the present work and the corresponding data on the enthalpies of sublimation recommended by Kovács and Konings (2003) for the series GdCl₃–LuCl₃ arise from the fact that the latter authors give preference to low-temperature heat capacity measurements performed by Tolmach et al. (Gorbunov et al., 1986; Tolmach et al., 1987c, 1988, 1990b,c,d) and use a different approach to taking into account the enthalpy of the liquid state.



FIGURE 25 Enthalpies of sublimation $\Delta_{sub}H^{\circ}(298)$: \blacksquare , recommended by Myers and Graves (1977b); \bullet , recommended by Kovács and Konings (2003); and \Box , recommended in this work.

6.4 Calculations of atomization enthalpies from appearance energies and equilibrium constants

The recommended enthalpies of sublimation (Tables 28–41; Figure 25) were used to calculate the enthalpies of atomization $\Delta_{at}H^{\circ}(\text{RCl}_3, 298)$ for comparison with similar data found by other independent methods such as electron-impact ionization or the measurement of gas-phase equilibria. The enthalpies of formation of lanthanides and atomic chlorine necessary for such calculations were taken from IVTANTERMO (2004), and the enthalpies of formation of crystalline RCl₃ from Table 27 (fifth column).

In addition, the enthalpies of atomization were calculated from the appearance energies of R^+ ions measured experimentally (Chervonnyi and Chervonnaya, 2004b,e,f; Evdokimov et al., 1984; Sapegin, 1984; Sapegin et al., 1982a, 1984) under the conditions of electron-impact-induced ionization of RCl₃ molecules.

At last, studies of the

$$2R(g) + 3EuCl_2(g) = 3Eu(g) + 2RCl_3(g)$$

and

$$2R(g) + 3BaCl_2(g) = 3Ba(g) + 2RCl_3(g)$$

reactions performed by Chervonnyi (1977a,b) allowed the equilibrium constants of these reactions to be calculated from the mass spectra recorded during the vaporization of the $R + EuCl_2$ (R = Nd, Gd, and

Dy) and R + BaCl₂ (R = Ce, Pr, Tb, Dy, Ho, Er, and Lu) mixtures. The equilibrium constants and enthalpies of formation of $EuCl_2$ and $BaCl_2$ were then used to calculate the enthalpies of atomization of several lanthanide trichlorides.

The low intensities of molecular ions observed under mass spectrum recording conditions forced the author to perform measurements at ionizing electron energies much higher than the threshold energies (~40 eV). The simultaneous occurrence of reactions with the formation of mono- and dichlorides in the gas phase resulted in the overlapping of the signals arising from ions formed in dissociative ionization and, which is most important, in ions formed from molecular precursors contributing to the intensity of the atomic ions R^+ (Ba⁺). The corresponding contributions were determined in the analysis of mass spectra performed by Chervonnyi (1977a) taking into account the limited data on pure lanthanide di- and trichlorides. In addition, the enthalpies of atomization obtained in this way depend on the reduced Gibbs energies of the compounds participating in the reaction and on the accepted enthalpy of atomization of the main reference compound BaCl₂ at the time these studies were performed. We found that all these factors substantially distort the results.

We consequently recalculated the enthalpies of atomization from the data we reported in 1977 (Chervonnyi, 1977a) using more recent data on the thermodynamic functions of atomic barium and lanthanides and barium dichloride (IVTANTERMO, 2004), of europium dichloride (Chervonnyi and Chervonnaya, 2003), and of lanthanide trichlorides (Chervonnyi and Chervonnaya, 2004g). We further used revised values for the enthalpies of atomization of EuCl₂ (Chervonnyi and Chervonnaya, 2004a, 2005b) and BaCl₂ (IVTANTERMO, 2004). Finally, we took into account the averaged mass spectrum of pure RCl₃ obtained from the totality of the mass spectra reported for these compounds (Chervonnyi, 1977a; Chervonnyi and Chervonnaya, 2004b; Chervonnyi et al., 1973, 1974, 1975; Ciach et al., 1973; Evdokimov et al., 1984; Hastie et al., 1968; Kapala et al., 1998; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1993b, 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a,b, 1999; Lisek et al., 1998a,b; Pogrebnoi et al., 2001) by describing the dependence of the intensities of the R^+ , RCl^+ , and RCl_3^+ ions on the number of the lanthanide in the series with a second-degree polynomial (the intensity of the RCl_2^+ ions was taken to be 100 arbitrary units, a.u.). This may well be not the best method for describing the individual mass spectra of RCl₃, but all of the available data, including multiple measurements of the mass spectra of all the lanthanide trichlorides (except PmCl₃) with a substantial spread of data, are indicative of a tendency toward an increase in the relative intensities of the R⁺ (from ~ 11 to ~ 27 a.u.), RCl⁺ (from ~ 8 to ~ 31 a.u.), and RCl₃⁺ ions (from ~ 5 to ~ 22 a.u.) as the number of R increases from LaCl₃ to LuCl₃.
Similar tendencies are observed in the mass spectra of the lanthanide dichlorides SmCl₂, EuCl₂, and YbCl₂ (Chervonnyi, 1975, 1977a; Chervonnyi et al., 1974; Evdokimov et al., 1984; Hariharan et al., 1972; Hastie et al., 1968; Khasanshin et al., 1998; Kudin et al., 1993a; Kuznetsov et al., 1997b; Pelipets et al., 2003; Pogrebnoi and Kudin, 2003a,b; Sapegin et al., 1982b). We ignored the completely erroneous results reported by Kudin et al. (1993b) who studied the high-temperature behavior of NdCl₂ and NdCl₃.

The enthalpies of atomization recalculated from the data (Chervonnyi, 1977a) are listed in Table 42. It was assumed in the calculations that $\Delta_{at}H^{\circ}$ (BaCl₂, 298) is equal to 926.905 kJ/mol (IVTANTERMO, 2004). We used the recommended enthalpy of atomization of EuCl₂, 899.291 kJ/mol (Chervonnyi and Chervonnaya, 2004a, 2005b) for calculating the

	$\Delta_{at} H^{\circ}(RCl_3,$	298)			
R	а	Ь	c	d	е
La	1525.2	1532.5	1535.4	_	_
Ce	1510.0	_	1513.9	_	1497.2
Pr	1447.6	_	1450.9	_	1449.4
Nd	1400.3	_	1408.0	1396.3	-
Pm	1324.8	_	_	_	-
Sm	1279.8	1278.0	1284.4	_	-
Eu	1200.5	_	_	_	-
Gd	1472.2	_	1476.9	1423.3	-
Tb	1452.3	_	1450.4	_	1446.0
Dy	1340.7	_	1348.7	1343.1	1342.6
Но	1358.3	_	1366.4	_	1374.7
Er	1370.8	_	1394.7	_	1405.4
Tm	1291.4	_	1296.5	_	-
Yb	1168.7	1167.9	1198.4	_	-
Lu	1470.2	_	-	_	1474.7

TABLE 42 Enthalpies of atomization of lanthanides trichlorides (kJ/mol)

^a Calculated from the enthalpies of sublimation recommended in this work.

^b Calculated from the appearance energies of R⁺ in the electron-impact-induced ionization of RCl₃ determined with errors of ±9.6 kJ/mol according to the authors (*Cheroonnyi and Cheroonnaya, 2004b,e,f*).

^c Calculated from the R⁺ ion appearance energies in the electron-impact-induced ionization of RCl₃ determined with errors of ±4 kJ/mol according to the authors (Sapegin et al., 1982a, 1984; Evdokimov et al., 1984; Sapegin, 1984). The ionization energies of 4f elements used in the calculations were those recommended by the National Institute of Standards, USA (NIST Ground Levels); data on the (H° (298) – H° (0)) values for 4f elements and atomic chlorine were from IVTANTERMO (2004), and the H° (298) – H° (0)) values for gaseous lanthanide trichlorides, from Chervonnyi and Chervonnava (2004e).

gaseous lanthanide trichlorides, from Chervonnyi and Chervonnaya (2004g). ^{*d*} Calculated from the mass spectra of vapor over the R + EuCl₂ systems (Chervonnyi, 1977a); according to the author, the error in the enthalpies of atomization was ±18 kJ/mol.

^e Calculated from the mass spectra of vapor over the R + BaCl₂ systems (Chervonnyi, 1977a); according to the author, the error in the enthalpies of atomization was ± 18 kJ/mol.

enthalpies of atomization of RCl₃ from the equilibrium constants of the reactions of Nd, Gd, and Dy with EuCl₂.

Several circumstances attract attention when we analyze the data presented in Table 42. First, the enthalpies of atomization found from the data of Sapegin et al. (1982a, 1984), Evdokimov et al. (1984), and Sapegin (1984) are all larger than those recommended in this work, with the exception of the enthalpy of atomization of TbCl₃. Some reasons for these discrepancies were mentioned previously (Chervonnyi and Chervonnaya, 2004a,b,e,f, 2005b). Next, similar exaggeration of the enthalpies of atomization was obtained after reprocessing the data from Chervonnyi (1977a) on HoCl₃ and ErCl₃. For ErCl₃, the difference was outside measurement errors. Conversely, the $\Delta_{at}H^{\circ}$ (298) value for GdCl₃ was strongly underestimated. These errors are of rather instrumental character because the subtraction of contributions gives small values that strongly distort equilibrium constant values.

On the whole, the majority of the results on the enthalpies of atomization (Chervonnyi and Chervonnaya, 2004b,e,f; Evdokimov et al., 1984; Sapegin, 1984; Sapegin et al., 1982a, 1984) are in satisfactory agreement with the corresponding values found from saturated vapor pressure measurements in spite of the complexity of the high-temperature behavior of these compounds, especially above their melting points.

6.5 Recommended enthalpy data for lanthanide trichlorides

Full sets of recommended data for standard temperature 298.15 K are listed in Table 43. The recommended enthalpies of sublimation were used to calculate the enthalpies of formation $\Delta_f H^{\circ}(\text{RCl}_3, \text{ g 298})$. The enthalpies of formation of crystalline RCl₃ necessary for such calculations were taken from Table 27 (fifth column).

The data obtained (see Table 43) allowed us to recalculate them for standard temperature 0 K using the needed parameters from IVTANTERMO (2004). These enthalpies are summarized in Table 44.

6.6 New saturated vapor pressure measurements for YbCl₃ and LuCl₃

After finishing this analysis, new data on YbCl₃ and LuCl₃ appeared (Brunetti et al., 2005), which allowed the range of the compounds used for estimating the reliability of the thermodynamic functions suggested by us to be broadened. At present, studies of virtually the whole series of lanthanide trichlorides (except PmCl₃ and EuCl₃) have been performed (Brunetti et al., 2000, 2003, 2004, 2005; Piacente et al., 2002, 2003; Scardala et al., 2003; Villani et al., 2000a,b, 2002).

R	⊿ _{sub} H°(298)	⊿ _f H°(cr, 298)	⊿ _f H°(g, 298)	∆ _{at} H°(298)
La	340.3	-1071.6 ± 1.5	-731.3	1525.2
Ce	331.1	-1060.1 ± 1.5	-729.0	1510.0
Pr	329.6	-1057.5 ± 1.5	-727.9	1447.6
Nd	331.8	-1041.1 ± 1.0	-709.3	1400.3
Pm	332.0	-1033.7 ± 10	-701.7	1324.8
Sm	315.0	-1025.3 ± 2.0	-710.3	1279.8
Eu	275.0	-935.4 ± 3.0	-660.4	1200.5
Gd	313.5	-1023.3 ± 1.5	-709.8	1472.2
Tb	308.3	-1010.6 ± 3.0	-702.3	1452.3
Dy	300.9	-992.4 ± 3.0	-691.5	1340.7
Ho	303.3	-997.5 ± 2.5	-694.2	1358.3
Er	302.4	-995.5 ± 2.0	-693.1	1370.8
Tm	301.5	-996.2 ± 2.5	-694.7	1291.4
Yb	306.9	-959.2 ± 3.0	-652.3	1168.7
Lu	305.8	-984.2 ± 2.5	-678.4	1470.2

TABLE 43 Enthalpies of sublimation, formation, and atomization, kJ/mol^a

 $^a\,$ The error in the enthalpies was estimated to ± 3 kJ/mol.

R	$\varDelta_{\sf sub} H^{\circ}(0)$	⊿ _f H°(cr, 0)	$\varDelta_{\rm f} H^{\circ}$ (g, 0)	$\varDelta_{at} H^{\circ}(0)$
La	341.150	-1071.720	-730.570	1519.773
Ce	331.906	-1060.253	-728.347	1506.207
Pr	330.390	-1058.421	-728.031	1443.891
Nd	332.553	-1042.315	-709.762	1396.622
Pm	332.733	-1034.268	-701.535	1320.395
Sm	315.732	-1023.775	-708.043	1271.903
Eu	275.760	-937.046	-661.286	1198.146
Gd	314.267	-1021.763	-707.496	1466.356
Tb	309.080	-1010.067	-700.987	1447.847
Dy	302.824	-993.868	-691.044	1337.904
Ho	305.140	-999.314	-694.174	1355.034
Er	304.198	-997.319	-693.121	1366.981
Tm	303.278	-998.156	-694.878	1287.738
Yb	308.648	-960.742	-652.094	1163.954
Lu	307.558	-984.900	-677.342	1464.202

TABLE 44 Enthalpies of sublimation, formation, and atomization, kJ/mol^a

^{*a*} All primary (experimental) enthalpy values are given with an accuracy of 0.1 kJ/mol. Other values calculated from them have an accuracy of 0.001 kJ/mol, as accepted in IVTANTERMO (2004).

Brunetti et al. (2005) have performed eight series of YbCl₃ saturated vapor pressure measurements by the torsion method during the sublimation of YbCl₃. In addition, six measurements of this parameter were made by the Knudsen integral method.

Calculations according to the third and second laws of thermodynamics based on torsion measurement results give the following values: 299.7, 301.5, 301.5, 300.8, 300.5, 301.1, 300.9, and 297.0 kJ/mol (III law) and 292.8, 297.1, 297.6, 293.7, 296.5, 294.2, 299.4, and 293.6 kJ/mol (II law). Averaging these values gives $\Delta_{sub}H^{\circ}$ (298, III law) = 300.4 ± 1.0 kJ/mol and $\Delta_{sub}H^{\circ}$ (298, II law) = 295. 6 ± 1.7 kJ/mol.

Calculations according to the third law of thermodynamics based on measurement by the Knudsen integral method give the following values: 294.7, 299.2, 296.6, 297.9, 301.9, and 299.7 kJ/mol. The mean $\Delta_{sub}H^{\circ}$ (298, III law) value for six effusion measurements is 298.3 \pm 2.0 kJ/mol. At the same time, $\Delta_{sub}H^{\circ}(298, \text{ II law})$ calculations from these six measurements give an obviously underestimated value of 260.0 ± 31.0 kJ/mol. Nevertheless, on the whole, measurements of saturated vapor pressures over YbCl₃ should be accepted as fairly reliable, considering the complex behavior of this compound at high temperatures (see Chervonnyi and Chervonnaya, 2004f). Brunetti et al. (2005) were able to obtain experimental torsion measurements according to which the difference between the $\Delta_{\rm sub}H^{\circ}(298)$ values calculated according to the second and third laws of thermodynamics is less than 5 kJ/mol. The enthalpy of sublimation obtained from these data ($\Delta_{sub}H^{\circ}(298, \text{III law}) = 300.4 \text{ kJ/mol}$) is slightly lower than that recommended by us in this work on the basis of the results of other measurements (306.9 kJ/mol).

The data obtained by Brunetti et al. (2005) for lutetium trichloride agree more closely with the recommendations made in this work. Indeed, calculations from the data obtained in a series of six torsion measurements yield the mean values $\Delta_{sub}H^{\circ}(298, \text{III law}) = 303.0 \text{ kJ/mol}$ and $\Delta_{sub}H^{\circ}(298, \text{III law}) = 305.6 \text{ kJ/mol}$. These values should, however, be corrected to take into account a comparatively high content of dimeric Lu₂Cl₆ molecules in the vapor phase.

The enthalpies of sublimation of $LuCl_3$ were calculated by Brunetti et al. (2005) taking this correction into account with the use of the data reported by Pogrebnoi et al. (1997), according to which the content of dimeric Lu_2Cl_6 molecules in saturated vapor is 20% at 1000 K. It was shown in our analysis of the thermodynamic properties of dimeric molecules of lanthanide trichloride in the gas phase (Chervonnyi and Chervonnaya, 2006) that the latter value was strongly exaggerated. It follows from the results obtained by Saloni et al. (2006) that, over the temperature range of studies performed by Brunetti et al. (2005), 942– 1075 K, the content of dimeric molecules was within the range 2–6%. Taking into account this value, calculations based on six series of torsion measurements give the mean values $\Delta_{sub}H^{\circ}(298, \text{III law}) = 303.3 \pm 0.3 \text{ kJ/mol and } \Delta_{sub}H^{\circ}(298, \text{II law}) = 303.2 \pm 1.6 \text{ kJ/mol. Separate enthalpy values for these series are 303.4, 303.3, 303.3, 302.9, 303.9, and 303.3 \text{ kJ/mol (III law) and 302.1, 301.0, 305.2, 301.1, 304.7, and 305.1 kJ/mol (II law). The value recommended in Table 43 is 305.8 kJ/mol.$

More recent data (Saloni et al., 2006) not considered above should also be mentioned. In this work, the authors report the results of two series of measurements of saturated vapor pressures over solid CeCl₃ and LuCl₃. Calculations of $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{sub}H^{\circ}(298, \text{II law})$ with the use of the thermodynamic functions recommended by us for these compounds give (kJ/mol): 332.4 and 333.4 (III law) and 326.9 and 341.4 (II law) for CeCl₃ and 304.0 and 303.1 (III law) and 319.6 and 308.7 (II law) for LuCl₃. The $\Delta_{sub}H^{\circ}(298, \text{III law})$ values determined from the results obtained by Saloni et al. (2006) closely agree with our recommendations.

The example of experimental data processing for LuCl₃ from (Brunetti et al., 2005) considered above substantiates our views on the optimum selection of the Debye characteristic temperature and Einstein characteristic frequencies used to calculate the temperature dependences of heat capacities.

To summarize, the calculations performed to determine the thermodynamic functions of RCl_3 in the condensed state and a systematic analysis of the use of these functions in calculations of the standard enthalpies of sublimation allowed us to compile a complete set of the thermodynamic parameters for modeling equilibria involving these compounds.

In addition, we were not only able to calculated data not reported (or calculated) before but also to suggest new values for monoclinic lanthanide trichlorides and to find out the reason for noticeable discrepancies between the thermodynamic characteristics of these compounds and the results reported in review articles (Kovács and Konings, 2003; Myers and Graves, 1977b). Additional proofs in favor of our approach to calculations of the thermodynamic functions of lanthanide halides will be presented after the description of these parameters for RCl₂.

7. THERMODYNAMIC PROPERTIES OF DIMERIC MOLECULES OF LANTHANIDE TRICHLORIDES

A survey of data shows that the major components of the saturated vapor over lanthanide trichlorides are monomeric RCl_3 molecules, whereas the content in R_2Cl_6 dimers is rather small (Chervonnyi and Chervonnaya, 2004b; Chervonnyi et al., 1973, 1974, 1975; Hastie et al., 1968; Kapala et al., 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a, 1999; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001; Polyachenok, 1972; Sapegin, 1984).

A further increase in the degree of association in vapor is less noticeable, although pentamers $(TmC1_3)_5$ and hexamers $(LuCl_3)_6$ have been identified in vapor over the corresponding trichlorides (Khasanshin et al., 2001a; Pogrebnoi et al., 1997).

Although the saturated vapor pressures of lanthanide trichloride associates were repeatedly measured and their enthalpies of sublimation $(\Delta_{sub}H^{\circ}(R_nCl_{3n}, 298))$ calculated from these data, their use in thermodynamic calculations presents definite difficulties. The $\Delta_{sub}H^{\circ}(R_nCl_{3n_{\ell}}298)$ values for the entire series of lanthanide trichlorides show a rather wide scatter, which prevents the selection of reliable values as well as the estimation of the trend in the change in these values along the series. Indeed, calculations of the enthalpies of sublimation of dimers from systematic tensiometric measurements of the saturated vapor pressure of these molecules showed that they increase in the series Tb₂Cl₆-Yb₂Cl₆ (Polyachenok, 1972). At the same time, processing (Pogrebnoi, 2004) of mass spectral data on vapor association over lanthanide trichlorides (Chervonnyi and Chervonnaya, 2004b; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a,b, 1999; Pogrebnoi et al., 2001) reveals an opposite tendency. The difference between the $\Delta_{sub}H^{\circ}(R_nCl_6, 298)$ values from Pogrebnoi (2004) and those we obtained by processing the data of Polyachenok (1972) can be as large as 100 kJ/mol.

These significant differences are likely caused by the incongruent sublimation (evaporation) of the compounds under the experimental conditions used (Chervonnyi and Chervonnaya, 2004a,g). This may be due to various factors. The first one is the extremely high hygroscopicity of lanthanide trichlorides, which react with moisture to form crystal hydrates RCl₃·*m*H₂O (m = 7 for La, Ce, and Pr; m = 6 for R = Nd–Lu; see, for instance, Kipouros and Sharma, 1990; Sokolova et al., 1981). On heating, these crystal hydrates partially lose water and evolve HCl to initially form more stable oxychlorides which eventually convert into oxides:

$$RCl_3 \cdot mH_2O \rightarrow ROCl + 2HCl + (m-1)H_2O \rightarrow R_2O_3$$

The second factor is the possible decomposition of lanthanide trichlorides at high temperature, especially in melts (see Goryushkin et al., 1990b; Laptev et al., 1986). The resulting nonstoichiometric condensed phase evaporates incongruently, and the activity of RCl₃ decreases, which leads to a decrease in the partial pressure of the monomer and, hence, to an even more noticeable decrease in the saturated vapor pressure of the dimer. As RCl₃ decomposes, dichlorides RCl₂ can appear in the vapor, as was found by Chervonnyi (1977a) for virtually the entire lanthanide series. Finally, it should be taken into account that the material of the container from which lanthanide trichlorides are evaporated can promote these processes. An example of a similar phenomenon was described by Lee et al. (1982).

Manifestations of the above processes can be judged from, for example, the available mass spectral data. The mass spectra of all trichlorides, except for PmCl₃ (the composition of the saturated vapor over PmCl₃ has not hitherto been studied) and EuCl₃ (discussed below), were repeatedly measured (Chervonnyi, 1975, 1977a; Chervonnyi and Chervonnaya, 2004b; Chervonnyi et al., 1973, 1974, 1975; Ciach et al., 1973; Evdokimov et al., 1984; Hastie et al., 1968; Kapala et al., 1998, 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1993b, 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a,b, 1999; Lisek et al., 1998a,b; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001). Six different measurements were carried out for NdCl₃ and five measurements for SmCl₃; two or three measurements were reported for other trichlorides, and the mass spectrum of ErCl₃ was only measured once by Evdokimov et al. (1984). The ion currents related to ionization of associates were not always measured in the cited works. However, the lack of any clear regular tendency in the available experimental mass spectra of lanthanide trichloride monomers is noteworthy. The scatter of relative ion currents in going from LaCl₃ to LuCl₃ is indeed large.

However, in our opinion, incongruent evaporation is more likely dictated by the purity of the initial compounds and the accuracy in preparing and carrying out the experiment. For example, the vapor composition over LaCl₃ was measured by Hastie et al. (1968) with high precision. The isothermal evaporation of SmCl₃ was found to be congruent (Chervonnyi et al., 1974). Our analysis of the thermodynamic characteristics of monomeric molecules RCl₃ showed that the most reliable saturated vapor pressures measured by the torsion method (Brunetti et al., 2000, 2003, 2004, 2005; Piacente et al., 2002, 2003; Scardala et al., 2003; Villani et al., 2000a,b, 2002) nearly for all lanthanide trichlorides (except for PmCl₃ and EuCl₃) are evidence of congruent sublimation (evaporation) of these compounds.

In this context, we attempted to determine the contents of the monomer and dimer molecules in the saturated vapor over lanthanide trichlorides by mass spectrometry (Chervonnyi and Chervonnaya, 2006), taking into account that, in a congruently evaporating system, the partial pressure of R₂Cl₆ can be determined without resorting to the vapor pressure of a reference, but simply by using the partial pressure of monomer molecules calculated from their thermodynamic characteristics (Chervonnyi and Chervonnaya, 2004g, 2007b,g).

We were also encouraged by the publication of the thermodynamic functions for $R_2Cl_6(g)$ (Gorokhov and Osina, 2005), which, in combination with the partial pressures of dimer molecules, make it possible to calculate standard thermodynamic characteristics of these molecules

and, thus, to obtain the full set of thermodynamic parameters required to describe numerically the equilibria involving these molecules.

7.1 Mass spectra

The specific features of electron-impact ionization of lanthanide trichloride monomers and dimers were first considered in studies of the sublimation of lanthanum trichloride and of a EuCl₃–LuCl₃ mixture by mass spectrometry (Hastie et al., 1968). The R⁺, RCl⁺, RCl⁺, and RCl⁺₃ ions were believed to originate from ionization of monomer molecules, whereas the appearance of La₂Cl⁺₅, Eu₂Cl⁺₅, EuLuCl⁺₅, and Lu₂Cl⁺₅ ions was direct evidence of the presence of dimeric molecules in the vapor. The dissociative ionization of monomer molecules mainly led to the loss of one chlorine atom; thus, the RCl⁺₂ ions were the most abundant, as seen from the mass spectra. This holds true for all mass spectra recorded later (including those in the present work) for this class of compounds, regardless of the type of mass spectrometer and ionizing electron energy used. Therefore, the intensity of the RCl⁺₂ line was, as a rule, taken as 100 a.u., while the intensities of the other lines were compared to this line.

The second important feature of the mass spectrum was that electronimpact ionization of dimeric molecules did not lead to the formation of the molecular ion $R_2Cl_6^+$. As in the case of monomer molecules, dissociative ionization of dimeric molecules mainly led to the loss of one chlorine atom (giving rise to $R_2Cl_5^+$ fragment ions). In some cases, weak lines of R_2^+ , R_2Cl^+ , $R_2Cl_2^+$, $R_2Cl_3^+$, and $R_2Cl_4^+$ ions were observed. In particular, in the vapor over SmCl₃, the Sm₂Cl₄⁺ ion was identified, its spectral intensity being 0.2 (Chervonnyi et al., 1973) or 0.1 (Pogrebnoi et al., 2001). In the mass spectrum of the saturated vapor over TbCl₃, the Tb₂Cl₃⁺ and Tb₂Cl₄⁺ intensities were found to be 0.01 and 0.15, respectively (Khasanshin et al., 1999). The Yb₂Cl₄⁺ ion,with an intensity of 0.2, was identified in vapor over ytterbium trichloride (Kudin et al., 1997a). In the mass spectrum of lutetium trichloride, which exhibits the highest degree of association, the Lu₂⁺ (0.02), Lu₂Cl⁺ (0.02), Lu₂Cl₂⁺(0.02), Lu₂Cl₃⁺ (0.03), and Lu₂Cl₄⁺ (0.65) ions were identified by Pogrebnoi et al. (1997).

In the calculations of partial pressures (Hastie et al., 1968), ionization of dimeric molecules accompanied by loss of more than one atom (especially in reaction steps that can interfere with ionization of monomers) was assumed to be improbable. This assumption was experimentally confirmed in studies of the congruent evaporation of $SmCl_3$ (Chervonnyi et al., 1974). Isothermal evaporation of a sample of known weight was carried out at several temperatures, and the saturated vapor pressure was determined by the Hertz–Knudsen equation. In each experiment, the state of an unsaturated vapor caused by the presence of an nonvolatile species (~1.5% $SmCl_2$) was determined in the end of evaporation and, with the use of the procedure described by Belousov et al. (1970), the mass spectrum coefficients b_{i2} were determined, which characterize the contribution of the dimer to the ion current intensity of the monomer (see Table 45).

Based on the data in Table 45, a conclusion was drawn that the contributions of dimers to the ion currents assigned to the ionization of monomers are negligibly small. Hence, the contents of dimers in the saturated vapor over lanthanide trichlorides can be calculated taking into account only the $R_2Cl_5^+$ ion current intensity. In further studies, this fact was not additionally verified. In calculations, it was automatically taken into account.

The mass spectra of the saturated vapor over lanthanide trichlorides we obtained (Chervonnyi and Chervonnaya, 2006) are presented in Table 46. The results of other works in which $R_2Cl_5^+$ ions have been identified are also compiled in this table.

The ion currents in Table 46 (from fourth to eighth columns) were corrected for the isotopic composition of the chemical elements. When a secondary electron multiplier (SEM) was used, corrections were applied for the dependence of the multiplier gain on the ion mass. We found that this gain is proportional to $M^{-0.5}$, where M is the mass of the ion (Chervonnyi and Chervonnaya, 2006). Taking into account this correlation and the relationship between pressure and the experimental ion current in mass spectral measurements, the partial pressure of dimers (P_d) was calculated by the formula

$$P_{\rm d} = \frac{P_{\rm m} \sigma_{\rm m} I_{\rm R_2 Cl_5^+}}{\sigma_{\rm d} (I_{\rm R^+} + I_{\rm RCl^+} + I_{\rm RCl_2^+} + I_{\rm RCl_3^+})}$$
(17)

where I_{R^+} , I_{RCl^+} , $I_{RCl^+_2}$, $I_{RCl^+_3}$, and $I_{R_2Cl_5^+}$ are the ion current intensities in the mass spectrum; σ_m and σ_d are the ionization cross sections of monomeric and dimeric molecules, respectively.

It follows from Eq. (17) that there is no need to determine the absolute values of the ionization cross sections σ_m and σ_d . It is sufficient to use their ratio σ_d/σ_m . It is worth noting that the problem of taking into account the

TABLE 45 Mass spectrum coefficients b_{i2} of samarium trichloride, data fromChervonnyi et al. (1974)

Т, К	<i>b</i> ₀₂ (Sm ⁺)	<i>b</i> ₁₂ (SmCl ⁺)	<i>b</i> ₂₂ (SmCl ₂ ⁺)	<i>b</i> ₃₂ (SmCl ₃ ⁺)
1138	0.00 ± 0.02	0.04 ± 0.02	0.00 ± 0.02	0.23 ± 0.12
1165	0.09 ± 0.02	0.01 ± 0.02	0.01 ± 0.02	0.29 ± 0.14
1187	0.00 ± 0.02	0.02 ± 0.02	0.02 ± 0.02	0.09 ± 0.04
1220	$\textbf{-0.16}\pm0.05$	0.00 ± 0.02	0.04 ± 0.02	0.11 ± 0.06

 $b_{i2} = I_{i/Sm_2Cl_6}/I_{Sm_2Cl_5}$, where I_{i/Sm_2Cl_6} is the intensity of the *i*th ion formed upon ionization of Sm₂Cl₆.

TABLE 46 Mass spectral data for saturated vapor over lanthanide trichlorides: experimental conditions (columns 2, 3), relative ion current intensities (columns 4–8), partial pressures of monomers and dimers (P_m and P_d , in Pa, columns 9, 10; see text for definitions), and enthalpies of reaction (18) in kJ/mol (column 12)

R	Т (К)	<i>E</i> (eV)	R^+	RCl^+	RCl_2^+	RCl_3^+	$R_2Cl_5^+$	P _m	P _d	References	$\Delta_{ m r}$ H $^{\circ}$ (298)
1	2	3	4	5	6	7	8	9	10	11	12
La	1030	50	~ 0.2	~ 0.2	100	1.5	0.17	0.065	7.18×10^{-5}	а	204.0
	1086	50	13.6	12.5	100	3.0	0.16	0.440	3.63×10^{-4}	<i>b,c</i>	194.4
	1195	25	1.6	16	100	3.0	1.70	7.885	0.0741	d	208.0
Ce	1063	50	12.1	10.6	100	5.0	0.39	0.596	0.00121	е	197.1
	1000		10.9	10.6	100	4.2	0.91	0.065	3.14×10^{-4}	f	211.7
	1075	50	12.9	11.3	100	4.0	0.45	0.880	0.00206	С	196.9
	1197	50	11.6	10.3	100	6.1	0.91	16.604	0.0787	е	195.5
	1130	25	1.4	17	100	3.3	2.10	3.781	0.0435	8	207.6
Pr	1107	70	15.2	11.8	100	1.9	0.5	2.209	0.00571	c,h	196.6
	1105	25	2.8	20	100	5.1	1.78	2.102	0.0195	8	208.5
Nd	1052	70	6.5	10.6	100	4.7	0.7	0.351	0.00135	c,i,j	208.9
	1245	25	5.1	21	100	2.6	2.12	33.20	0.365	8	208.5
Sm	1070	25	2.0	16.6	100	4.3	2.9	2.321	0.0365	k	210.7
	1187	40	49.0	14.3	100	5.7	4.6	33.069	0.600	1	207.5
	1100	30	42.6	20.0	100	8.0	5.2	4.875	0.0991	m	211.9
	989	75	22.5	9.0	100	8.6	2.17	0.242	0.00250	е	210.8
	1109	75	20.0	8.0	100	7.3	4.72	6.038	0.140	с,е	212.8
	1110	25	20.1	22	100	2.7	3.89	6.182	0.111	8	210.3

(continued)

R	Т (К)	<i>E</i> (eV)	R^+	RCl^+	RCl_2^+	RCl_3^+	$R_2Cl_5^+$	P _m	Pd	References	$\Delta_{ m r}$ H $^{\circ}$ (298)
1	2	3	4	5	6	7	8	9	10	11	12
Gd	1055	30	21.4	14.5	100	13.4	4.9	1.231	0.0269	c,n	219.3
	1243	25	1.6	16	100	3.9	4.30	80.860	1.91	8	213.5
Tb	1047	40	29.1	15.2	100	12.2	5.5	1.573	0.0369	с,0,р	217.1
	1010	25	7.1	13.5	100	8.2	1.9	0.548	0.00539	0	211.4
	1120	25	1.8	15	100	5.4	3.93	10.041	0.215	8	213.2
Dy	1008	25	5.9	16.7	100	12.4	7.4	0.504	0.0184	<i>c,q,r,s</i>	223.6
2	1000		20.4	10.9	100	12.1	7.55	0.395	0.0139	f	223.6
	1096	25	6.0	19.0	100	4.7	5.38	5.646	0.156	8	217.5
Но	997	24	3.9	24.0	100	13.7	10.0	0.425	0.0200	<i>c,s,t</i>	226.1
	1105	25	3.0	18.0	100	5.6	6.83	8.122	0.292	8	219.7
Er	1065	30	17.7	15.1	100	18.3	15.2	4.077	0.273	С	225.1
	1085	25	1.8	15.5	100	7.3	6.80	6.763	0.246	8	219.0
Tm	1007	30	17.6	15.3	100	20.9	11.9	0.796	0.0410	с,р,и	226.5
	1067	25	8.7	25	100	7.9	10.40	5.244	0.257	8	222.1
Yb	1063	40	27.0	41.4	100	10.0	3.2	2.680	0.0320	1	216.5
	973	30	30.0	39.6	100	12.1	4.0	0.133	0.00195	m	225.1
	1072	30	13.9	46.0	100	14.8	0.5	3.513	0.00670	r	199.4
	1189	25	11.7	51.9	100	14.9	0.5	64.743	0.121	С	190.7
	1085	25	14.6	23.0	100	9.3	3.81	5.149	0.0890	8	218.1

 TABLE 46 (continued)

Lu	960	50	70	35	100	26	11	0.093	0.00294	а	232.0
	1056	90	13.9	13.6	100	38.1	26.0	2.412	0.252	C S V / /	235.9
	1068	25	3.3	18	100	7.7	10.30	3.469	0.185	8	229.2

^{*a*} Hastie et al. (1968). ^{*b*} Kudin et al. (2003b).

^b Kudin et al. (2003b).
^c Pogrebnoi (2004).
^d Chervonnyi and Chervonnaya (2004b).
^e Pogrebnoi et al. (2001).
^f Kapala et al. (2002).
^g Chervonnyi and Chervonnaya (2006).
^h Kudin et al. (2003a).
ⁱ Kudin and Smirnov (2003b).
^j Kudin and Smirnov (2003b).
^j Kudin and Smirnov (2003a).
^k Chervonnyi et al. (1973).
ⁱ Chervonnyi et al. (1975).
^m Sapegin (1984).
ⁿ Khasanshin et al. (2001b).
^o Khasanshin et al. (1999).

^o Khasanshin et al. (1999).

^p Kudin et al. (2000).

^{*q*} Kuznetsov et al. (1997a).

^r Kudin et al. (1997a).

^s Kudin et al. (1997b).

^t Kuznetsov et al. (1999).

" Khasanshin et al. (2001a).

^v Pogrebnoi et al. (1997).

absolute and relative ionization cross sections when converting ion currents to partial pressures was considered in the in-depth analysis of possible errors in measurements of partial pressures with the use of high-temperature mass spectrometry (Drowart et al., 2005). In particular, based on the corresponding data for alkali-metal halides, the ratio $\sigma_d/\sigma_m = 1.25 \pm 0.35$ was recommended. However, it follows from the experimental data surveyed in the review by Drowart et al. (2005) that this ratio is somewhat higher for chlorides and coincides with the value 1.5 recommended by Hilpert (1990). All partial pressures P_d in Table 46 were determined using the ratio $\sigma_d/\sigma_m = 1.5$ and P_m calculated by the third law according to Chervonnyi and Chervonnaya (2004g, 2007b,g) at the temperature at which mass spectra were recorded.

The reliability of measurements of the partial pressures of R₂Cl₆ can in principle be verified by a standard procedure based on changes in the thermodynamic characteristics of these molecules along the lanthanide series. However, the enthalpy of atomization $\Delta_{at}H^{\circ}(298)$ is not the most convenient parameter for such a check since it does not vary monotonically with the number of the lanthanides in the series. The plot of this dependence is a broken line with maxima at lanthanum, gadolinium, and lutetium compounds and minima at europium and ytterbium compounds. In addition, the enthalpy of atomization usually increases in going from dysprosium to erbium dimers.

As we found for lanthanide trifluorides and trichlorides (Chervonnyi and Chervonnaya, 2007a,g), the plot of the enthalpy of sublimation versus the number of the lanthanide is smoother. However, a simpler dependence should be valid for dimers when the enthalpies of the gas-phase reaction

$$R_2Cl_6(g) = 2RCl_3(g) \tag{18}$$

are compared. The R₂Cl₆ molecules have point group of symmetry D_{2h} (Gorokhov and Osina, 2005; Hargittai, 2005). Therefore, the dissociation of the bond between the lanthanide atom and the bridging chlorine atom in reaction (18) does not change the number of f electrons. Hence, the curve of the enthalpy of reaction (18) $\Delta_r H^{\circ}$ (298) as a function of the number of the lanthanide in the series should be a smooth one influenced only by the lanthanide contraction effect.

7.2 Thermodynamic functions

In calculations of $\Delta_r H^{\circ}(298)$, we used the thermodynamic functions of gaseous monomers described in Section 2. As for the dimers, we recalculated the thermodynamic functions reported by Gorokhov and Osina

(2005) for most molecules. This was caused by the way the electronic contribution to them was taken into account. With regard to the ionic character of bonding in the lanthanide compounds under consideration, it was assumed that the low-lying excited states in RX_3 are in adequation with the same states for the corresponding R^{3+} ion. Therefore, this contribution for the monomers was calculated from the energies of separate excited electronic states and their statistical weights inherent to each R^{3+} ion.

In Gorokhov and Osina (2005), the electronic component for R_2Cl_6 was found in some cases by using the energies obtained from *ab initio* calculations (Tsuchia et al., 1999) for the corresponding monomers (CeCl₃, PrCl₃, SmCl₃, EuCl₃, TbCl₃, and YbCl₃). For the other dimers R_2Cl_6 (R = Nd, Pm, Dy, Ho, Er, and Tm), only the data of Morrison and Leavitt (1982) on the splitting of the ground electronic state of R^{3+} was taken into account by Gorokhov and Osina (2005). In all cases, the energies of relatively highlying states (up to 10,000 cm⁻¹) were taken from Martin et al. (1978).

To eliminate unwanted errors in the calculation of the enthalpy of reaction (18), appropriate corrections were applied to the data of Gorokhov and Osina (2005). Inasmuch as the electronic contribution for dimeric molecules is twice the contribution for the monomers, the electronic contribution of the former was calculated from the energies of individual excited electronic states and their statistical weights described in Section 2 for RCl₃(g).

After this procedure was performed, the Gibbs energies for Pr_2Cl_6 , Sm_2Cl_6 , Eu_2Cl_6 , Tb_2Cl_6 , and Yb_2Cl_3 reported in (Gorokhov and Osina, 2005) were found to be noticeably different. This difference is maximum at 298.15 K and can be as large as $\sim 14 \text{ J/(mol}\cdot\text{K})$ in the case of Yb_2Cl_6 . The difference decreases with increasing temperature. For example, at 1500 K and higher temperatures, the difference is zero for Pr_2Cl_6 and nearly zero for Sm_2Cl_6 . For the other R_2Cl_6 molecules (R = Nd, Pm, Dy, Ho, Er, and Tm), the difference from the data of Gorokhov and Osina (2005) is small: it amounts to no more than $\sim 0.8 \text{ J/(mol}\cdot\text{K})$ at 298.15 K and also vanishes with increasing temperature.

The results of our calculation of the thermodynamic functions for the R_2Cl_6 molecules are presented in Table A7 in the form of the f_i coefficients (see Appendix). It is worth noting that in the calculation of the approximating coefficients for describing the reduced Gibbs energy, we used the molecular constants and the products of the principal moments of inertia of the R_2Cl_6 molecules from Gorokhov and Osina (2005). Therefore, the values of these approximating coefficients for La₂Cl₆, Gd₂Cl₆, and Lu₂Cl₆ coincide with those in Gorokhov and Osina (2005), since the electronic component for the RCl₃ monomers was calculated analogously, that is, taking into account only the degeneracy of the ground state.

7.3 Calculation of $\Delta_r H^{\circ}(298)$ from mass spectra

The calculation of $\Delta_r H^{\circ}(298)$ by the third law with the use of the partial pressures P_m and P_d listed in Table 46 showed that they are rather close to each other. As a rule, the differences in $\Delta_r H^{\circ}(298)$ values for the same compound are within ~5 kJ/mol, and their behavior as a function of the number of the central atom in the lanthanide series can be described by a second-degree polynomial. The only exceptions are obviously underestimated data obtained from the mass spectra of lanthanum, cerium, and praseodymium trichlorides (Kudin et al., 2003b; Pogrebnoi, 2004). It is worth noting that processing of five different measurements of the mass spectrum of the saturated vapor over ytterbium trichloride gave values in the range 190.7–225.1 kJ/mol. Despite the fact that some of these values were in agreement with the above dependence, we decided to exclude all experimental data on YbCl₃ from the data set used for analytical description of this dependence.

Thus, the coefficients of the second-degree polynomial were determined based on 30 of the 40 available $\Delta_r H^{\circ}(298)$ values, including the data obtained by processing the mass spectrum of lutetium trichloride after its sublimation from an EuCl₃–LuCl₃mixture (Hastie et al., 1968). This treatment shows that the enthalpy of reaction (18) for each of the lanthanide trichlorides (except europium trichloride) can be calculated by the following equation:

$$\Delta_r H^{\circ}(298) = 206.76946 + 0.17946n + 0.10049n^2 \tag{19}$$

where n = 1-15 for the series R = La-Lu.

For all processed data, the standard deviation of their arithmetic mean from the values determined by Eq. (19) is ± 0.54 kJ/mol, which demonstrates their rather high reproducibility.

7.4 Calculation of $\Delta_r H^{\circ}$ (298) from saturated vapor pressure measurements

The partial pressures of the monomers and dimers were presented either in tabulated or in analytical form (semilogarithmic representation) and, sometimes, in both forms (Chervonnyi and Chervonnaya, 2004b; Chervonnyi et al., 1973, 1974, 1975; Hastie et al., 1968; Kapala et al., 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a, 1999; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001; Polyachenok, 1972; Sapegin, 1984). All data, except those in Polyachenok (1972), were obtained from mass spectral measurements. The sensitivity constant of a mass spectrometer was determined from the weight loss of a reference compound during its isothermal evaporation (Chervonnyi et al., 1974; Hastie et al., 1968; Kapala et al., 2002). The reference was always silver with sometimes, in addition, RbCl, CsCl, CsBr, or CsI (Chervonnyi and Chervonnaya, 2004b; Chervonnyi et al., 1973, 1975; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a, 1999; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001; Sapegin, 1984).

Inasmuch as the saturated vapor pressures of the monomers and dimers were measured in different temperatures ranges, we used the following scheme of calculation: First, the standard enthalpies of sublimation of the dimers $\Delta_{sub}H^{\circ}(D, 298)$ were estimated by the second and third laws using the thermodynamic functions of the condensed state (Chervonnyi and Chervonnaya, 2007b). Then the $\Delta_{r}H^{\circ}(298)$ values were determined from the enthalpies $\Delta_{sub}H^{\circ}(M, 298)$ and $\Delta_{sub}H^{\circ}(D, 298)$ by the formula

$$\Delta_{\rm r} H^{\circ}(298) = 2\Delta_{\rm sub} H^{\circ}({\rm M}, 298) - \Delta_{\rm sub} H^{\circ}({\rm D}, 298)$$
(20)

The values of the standard enthalpies of monomeric lanthanide trichlorides $\Delta_{sub}H^{\circ}(M, 298)$ from Chervonnyi and Chervonnaya (2007g) were substituted into Eq. (20). When available (Chervonnyi and Chervonnaya, 2004b; Chervonnyi et al., 1973, 1974, 1975; Hastie et al., 1968; Kapala et al., 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a, 1999; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001; Polyachenok, 1972; Sapegin, 1984) tabulated P_d values were used in our calculations; otherwise, semilogarithmic representations were used (Khasanshin et al., 2001a; Kudin and Smirnov, 2003a; Kudin et al., 1997a,b, 2000; Kuznetsov et al., 2001a; Kudin and Smirnov, 2003a; Kudin et al., 1997a,b, 2000; Kuznetsov et al., 1997a; Pogrebnoi, 2004).

The results of these calculations are summarized in Table 47. Column " $\Delta_r H^{\circ}(298, \text{ II law})$ " shows the enthalpy values found according to the second law of thermodynamics. In column " $\Delta_r H^{\circ}(298, \text{ III law})$ " the enthalpy values were calculated according to the third law of thermodynamics. Moreover, the available enthalpy values calculated from the saturated vapor pressures over the α phase (specified as " α ") and calculated from the saturated vapor pressures over the melt (specified as "liq") are listed in separate columns.

Data reported in Table 47 show that the $\Delta_r H^{\circ}(298)$ values calculated by the second and third laws from the results of systematic tensiometric measurements of saturated vapor pressures presented in the semilogarithmic representation (Polyachenok, 1972) differ from each other by no more than 15 kJ/mol. However, variation of $\Delta_r H^{\circ}(298)$, calculated by the third law, as a function of the number of the lanthanide in the series sharply increases for gadolinium and terbium, then decreases in going down the series from Dy to Yb, and finally increases again for lutetium.

	$\Delta_{ m r}$ H $^{\circ}$ (298	3, 11 law)	$\Delta_{ m r}$ H $^{\circ}$ (298	3, III law)	
R	α	liq	α	liq	References
La	215.7 ^a	-	-	-	Hastie et al. (1968)
	_	212.9	-	212.1	Polyachenok (1972)
	190.5 ^b	-	196.6	-	Kudin et al. (2003b)
	197.5	-	195.8	-	Pogrebnoi (2004)
Ce	-	207.2	_	208.5	Polyachenok (1972)
	197.8	_	183.4	_	Pogrebnoi et al. (2001)
	347.5	_	198	_	Kapala et al. (2002)
	199	_	192.3	-	Pogrebnoi (2004)
Pr	_	193.6	_	185.8	Polyachenok (1972)
	351.8	_	202.2	199.3	Kapala et al. (2002)
	-	185.3	-	171.6	Kudin et al. (2003a) and Pogrebnoi (2004)
Nd	_	174 9	_	179 2	Polyachenok (1972)
Ita	_	167.8	201	203.4	Kapala et al. (2002)
	_	184.9	193.0°	188.4	Kudin and Smirnov (2003b)
	-	197.8	_	188.5	Kudin and Smirnov (2003a) and Pogrebnoi (2004)
Nd	_	170.0	_	179 7	Polyachenok $(1972)^d$
Sm	_	162.2	_	167	Polyachenok (1972)
om	_	209.6	_	-	$\frac{1972}{1973}$
	_	205.0	_	211 3	Chervonnyi et al. (1974)
		190.3		211.5	Pogrebnoi et al. $(2001)^e$
	_	206	_	107.1	Pogrobnoj et al $(2001)^e$
	_	200	_	201.8	Pogrebnoj (2004)
F 11		149.4		201.0 157.5	Polyachenok $(1972)^d$
Cd	_	149.4	_	107.3	Polyachenok (1972)
Gu	_	204.5	_	201	Khasanshin et al. (2001b) and Pogrebnoi (2004)
Th	_	1954	_	209 1	Polyachenok (1972)
10	_	240.4^{f}	_	220.6°	Khasanshin et al. (1999)
	_	210.1	_	219.1	Kudin et al. (2000)
	_	211.7	_	215.6	Pogrebnoj (2004)
Dv	_	190.1	_	197 5	Polyachenok (1972)
Dy	207.9	206.7	213.6	213.3	K_{11} retsolvet al. (1997a) and
	207.9	200.7	215.0	210.0	Kudin et al. (1997a,b)
	-	285	-	217	Kapala et al. (2002)
	-	216.6	-	203.3	Pogrebnoi (2004)
Но	_	172.4	-	185.2	Polyachenok (1972)

TABLE 47 Enthalpies of the reaction $R_2Cl_6(g) = 2RCl_3(g)$ (kJ/mol)

(continued)

$\Delta_{ m r}$ H $^{\circ}$ (298, II law		3, 11 law)	$\Delta_{ m r}$ H $^{\circ}$ (298	3, III law)	
R	α	liq	α	liq	References
	247.6	212.1	232.7	232.4	Kudin et al. (1997b) and Kuznetsov et al. (1999) ^g
	-	-	230.1	219.9	Kuznetsov et al. $(1999)^h$
Er	_	160.2	_	174.1	Polyachenok (1972)
	209.2	_	220.9	_	Pogrebnoi (2004)
Tm	-	144.5	-	159	Polyachenok (1972)
	220.5	-	225.4	-	Khasanshin et al. (2001a)
	207.5	-	205.1	-	Pogrebnoi (2004)
Yb	-	138.2	-	152.2	Polyachenok (1972) ^d
Lu	_	220.8	_	233.4	Polyachenok (1972)
	179.7	_	246.6	_	Kudin et al. (1997b)
	202.3 ⁱ	_	218.3 ⁱ	_	Pogrebnoi et al. (1997)
	178.8	-	199.9	-	Pogrebnoi (2004)

 TABLE 47 (continued)

^{*a*} Digitizing the plot of the product of the La₂Cl₅⁺ ion current by temperature versus reciprocal temperature (Hastie et al., 1968) makes it possible to calculate the enthalpy of sublimation of dimeric molecules ($\Delta_{sub}H^{\circ}$ (D, 1064) = 414.4 kJ/mol), from which $\Delta_{sub}H^{\circ}$ (D, 298) = 445.4 kJ/mol was calculated by the second law, and this value was used for the determination of $\Delta_{r}H^{\circ}$ (298).

^b Three different $\Lambda_{sub}H^{p}(D, 298)$ values can be calculated by the second law from the results of Kudin et al. (2003b): (i) from the logarithmic dependence of the product of the La₂Cl₃⁺ ion current by temperature versus reciprocal temperature (536.4 kJ/mol); (ii) by processing the experimental vapor pressure of the dimer (13 data points) (486.3 kJ/mol); and (iii) from the semilogarithmic representation reported in Kudin et al. (2003b) (499.1 kJ/mol). The $A_{2}FI(298)$ value was obtained using $\Lambda_{sub}H^{2}(D, 298) = 486.3$ kJ/mol.

^c Calculated from two experimental P_d values that correspond, according to data for the melting point of NdCl₃ (see Chervonnyi and Chervonnaya, 2007b), to the sublimation of this compound.

 d Calculated from estimates of the saturated vapor pressure (P_{m} and P_{d}) as a function temperature.

^e The vapor pressures of dimer molecules over the SmCl₃ melt were measured in two different experiments (Pogrebnoi et al., 2001). These data were processed separately and summarized in Table 47 on different lines. The thermochemical parameters obtained based on these measurements are noticeably different.

^{*f*} In Khasanshin et al. (1999), five separate series of experiments were performed to determine P_m and P_d . We calculated the standard enthalpies of sublimation for each of these series; then, average values were found and used in the calculation of $\Delta_r H^{\circ}$ (298).

 g Calculation of the saturated vapor pressure (Kudin et al., 1997b; Kuznetsov et al., 1999) ($P_{\rm m}$ and $P_{\rm d}$) as a function of temperature.

^{*h*} Calculations were performed based on the saturated vapor pressures at different temperatures (Kuznetsov et al., 1999). For the monomer, there are 27 measurements of the vapor pressure over the α phase and three measurements over the melt; for the dimer, there are two measurements of the vapor pressure over the α phase and three over the melt.

The standard enthalpies of sublimation of lutetium trichloride as monomers and dimers used in calculation of these quantities were calculated from the partial pressures $P_{\rm m}$ and $P_{\rm d}$ reported in Pogrebnoi et al. (1997).

This behavior is not consistent with mass spectral observations, although the enthalpies of reaction (18) in vapor over $LaCl_3$, $CeCl_3$, $TbCl_3$, and $LuCl_3$ are rather close to the values obtained by processing the mass spectral data.

Table 47 also shows that the scatter of the $\Delta_r H^{\circ}(298)$ values is considerably larger than the scatter observed in processing mass spectral data

(Kapala et al., 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a, 1999; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001). For example, the standard deviation of the arithmetic mean of the values found by Eq. (19) is ± 15.0 kJ/mol for the data estimated by the second law for sublimation and ± 5.9 kJ/mol for the values found by the second law for evaporation. The same deviations obtained in calculations by the third law are ± 3.6 (sublimation) and ± 3.3 (evaporation) kJ/mol. A major source of these differences can be detected by comparing the P_m/P_d ratios found from the measurements (Kapala et al., 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a, 1999; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001).

7.5 Calculation of P_m/P_d ratio

The calculated data are summarized in Table 48. The values in the third column have been determined from the partial pressures of the saturated vapor and those in the fourth column, from the mass spectra (Kapala et al., 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a, 1999; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001).

For calculating the ratios presented in the third column, log P = A - B/T relationships were preliminarily determined by least-squares processing of the experimental pressures of the saturated vapor of monomer and dimer molecules, and, then, the P_m/P_d ratio was calculated at the temperature at which the mass spectra were recorded. However, the data required for such a calculation are sometimes lacking (Khasanshin et al., 2001a; Kudin and Smirnov, 2003a; Kudin et al., 1997a,b, 2000; Kuznetsov et al., 1997a; Pogrebnoi, 2004). In these cases, the P_m/P_d ratio was calculated from the semilogarithmic representations reported in these works.

In agreement with Eq. (17), the partial pressure ratios presented in the fourth column are determined by the equation

$$\frac{P_{\rm m}}{P_{\rm d}} = \frac{\sigma_{\rm d}(I_{\rm R^+} + I_{\rm RCl^+} + I_{\rm RCl_2^+} + I_{\rm RCl_3^+})}{\sigma_{\rm m}I_{\rm R_2Cl_5^+}}.$$
(21)

It is worth noting (see Table 48) that, only in six cases, namely for CeCl₃ (Pogrebnoi, 2004), SmCl₃ (Pogrebnoi et al., 2001), GdCl₃ (Khasanshin et al., 2001b), TbCl₃ at 1010 K (Khasanshin et al., 1999), HoCl₃ (Kuznetsov et al., 1999), and ErCl₃ (Pogrebnoi, 2004), the P_m/P_d ratios in the third and fourth columns are identical or rather close to each other. For the other lanthanide trichlorides, however, the difference is very significant.

R	Т (К)	$P_{\rm m}/P_{\rm d}$		References
1	2	3	4	5
La	1086	909 ^{a,b}	1210	Kudin et al. (2003b) and Pogrebnoi (2004)
Ce	1063	4323 ^c	491	Pogrebnoi et al. (2001)
	1000	307 ^d	207	Kapala et al. (2002)
	1075	447 ^b	427	Pogrebnoi (2004)
Pr	1107	1372 ^e	387	Kudin et al. (2003a) and Pogrebnoi (2004)
Nd	1052	205 ^f	261	Kudin and Smirnov (2003a,b) and Pogrebnoi (2004)
Sm	989	103 ⁸	97	Pogrebnoi et al. (2001)
	1109	176 ^h	43	Pogrebnoi et al. (2001)
	1109	58 ^b	43	Pogrebnoi (2004)
Gd	1055	49 ⁱ	46	Khasanshin et al. (2001b)
	1055	54 ^b	46	Pogrebnoi (2004)
Tb	1047	96 ⁱ	43	Khasanshin et al. (1999)
	1010	102 ^j	102	Khasanshin et al. (1999)
Tb	1047	76 ^k	43	Kudin et al. (2000)
	1047	117 ^b	43	Pogrebnoi (2004)
Dy	1000	22^d	28	Kapala et al. (2002)
	1008	19 ¹	27	Kuznetsov et al. (1997a) and Kudin et al. (1997a,b)
	1008	58 ^b	27	Pogrebnoi (2004)
Но	997	12 ^m	21	Kudin et al. (1997b)
	997	21 ⁿ	21	Kuznetsov et al. (1999)
Er	1065	13 ^b	15	Pogrebnoi (2004)
Tm	1007	9°	19	Kudin et al. (2000) and Khasanshin et al. (2001a)
	1007	41 ^b	19	Pogrebnoi (2004)
Lu	1056	2 ^p	10	Kudin et al. (1997b)
	1056	14 ⁹	10	Pogrebnoi et al. (1997)
	1056	108 ^b	10	Pogrebnoi (2004)

TABLE 48Ratio of the partial pressures of dimer and monomer molecules in thesaturated vapor over lanthanide trichlorides

^{*a*} Calculated from a semilogarithmic representation based on 25 measurements of the saturated vapor pressure for the monomer and 15 measurements for the dimer (Kudin et al., 2003b).

Postel for the saturated vapor pressures ($P_{\rm m}$ and $P_{\rm d}$) as a function of temperature reported by Pogrebnoi (2004).

^c The $P_{\rm m}$ and $P_{\rm d}$ values were found from the semilogarithmic representation of 19 measurements of the saturated vapor pressure for the monomer and 14 measurements for the dimer reported by Pogrebnoi et al. (2001).

^d For calculation of $P_{m\nu}$ the dependence of the saturated vapor pressure from Kapala et al. (2002) was used; P_d was calculated from a similar dependence that we determined based on 14 measurements of P_d in this work for CeCl₃ and based on 8 measurements of P_d over the DyCl₃ melt.

^{*e*} Calculated from the dependences of the saturated vapor pressure (*P*_m and *P*_d) on temperature reported by Kudin et al. (2003a) and Pogrebnoi (2004).

- f Calculatied from the dependences of the saturated vapor pressure ($P_{\rm m}$ and $P_{\rm d}$) on temperature reported by Kudin and Smirnov (2003a) and Pogrebnoi (2004), and the processing of 17 measurements of saturated vapor pressure for the monomer and 30 measurements for the dimer reported by Kudin and Smirnov (2003a).
- g The $P_{\rm m}$ and $P_{\rm d}$ values were found from the semilogarithmic representation of 14 measurements of the saturated vapor pressure for the monomer and 8 measurements for the dimer reported (Pogrebnoi et al., 2001) for the first series of runs.
- ^{*h*} The $P_{\rm m}$ and $P_{\rm d}$ values were found from the semilogarithmic representation of 15 measurements of the saturated vapor pressure for the monomer and 23 measurements for the dimer (Pogrebnoi et al., 2001) for the second series of runs.
- ^{*i*} By processing 25 measurements of the saturated vapor pressure for the monomer and 15 measurements for the dimer (Khasanshin et al., 2001b).
- ^{*j*} In (Khasanshin et al., 1999), five separate series of experiments were performed to determine P_m and P_d . The first series: 10 measurements of P_m and 12 measurements of P_d . The second series: 10 measurements of P_m and 11 measurements of P_d . The third series: 12 measurements of P_m and 12 measurements of P_d . The fourth series: 9 measurements of P_d and 12 measurements of P_d . The furth series: 9 measurements of P_d . The average P_m/P_d ratio for these five series is given. See text for the results for each of the series.
- ^k Calculated from the saturated vapor pressures ($P_{\rm m}$ and $P_{\rm d}$) as a function of temperature reported by Kudin et al. (2000).
- ¹ Calculated from the saturated vapor pressures (P_m and P_d) as a function of temperature reported by Kuznetsov et al. (1997a) and Kudin et al. (1997a,b).
- ^{*m*} Calculated from the saturated vapor pressures ($P_{\rm m}$ and $P_{\rm d}$) as a function of temperature reported by Kudin et al. (1997b).
- ^{*n*} Since the mass spectrum was measured for saturated vapor over the melt, the three available measurements of the saturated vapor pressures for the monomer and dimer over the melt (Kuznetsov et al., 1999) were processed. The other P_m and P_d values in Kuznetsov et al. (1999) were measured in the course of sublimation of α -HoCl₃.
- o Calculated from the saturated vapor pressures ($P_{\rm m}$ and $P_{\rm d}$) as a function of temperature reported by Kudin et al. (2000) and Khasanshin et al. (2001a).
- ^{*p*} Calculated from the saturated vapor pressures (P_m and P_d) as a function of temperature reported by Kudin et al. (1997b).
- ^q By processing 13 measurements of the saturated vapor pressure for the monomer and 12 measurements for the dimer (Pogrebnoi et al., 1997).

Yet another specific feature of these data is that when the P_m/P_d ratios obtained by processing the mass spectral data are the same, the ratios found from measurements of saturated vapor pressures are considerably different. This is especially pronounced for LuCl₃ (Kudin et al., 1997b; Pogrebnoi, 2004; Pogrebnoi et al., 1997): the P_m/P_d ratio determined from mass spectra is 10 (fourth column), whereas three different P_m/P_d values amounting to 2 (data from Pogrebnoi et al., 1997), 14 (data from Kudin et al., 1997b), and 108 (data from Pogrebnoi, 2004) are given in the third column.

One possible reason for such the discrepancy between the P_m/P_d values found from the semilogarithmic representations and mass spectral data is that the evaporation of the samples is incongruent. This is demonstrated by measuring the pressures of the saturated vapor over samarium trichloride (Pogrebnoi et al., 2001) and terbium trichloride (Khasanshin et al., 1999).

For TbCl₃, five runs (presumably successive) of measurements of the $P_{\rm m}$ and $P_{\rm d}$ pressures were reported (Khasanshin et al., 1999). The $P_{\rm m}/P_{\rm d}$ ratios calculated for each of the runs successively increases from run to run: at T = 1047 K, this ratio is 67, 73, 96, 96, and 107, respectively; at T = 1010 K, the ratio is 80, 83, 97, 105, and 118, respectively.

Analogously, the data for SmCl₃ (Pogrebnoi et al., 2001) show that as the temperature increases from 989 to 1109 K, the P_m/P_d ratio found from the mass spectral data monotonically decreases since the content in dimeric molecules in the vapor increases with temperature. At the same time, the data in the third column of Table 48 show that P_m/P_d values are higher in the second run of experiments.

The fact that P_m/P_d values found from semilogarithmic representations are sometimes higher and sometimes lower than the ratios calculated from mass spectral data can be explained in some way. However, there is no way of explaining why the ratios of the contents of monomers and dimers in the saturated vapor over lutetium trichloride (Kudin et al., 1997b; Pogrebnoi, 2004; Pogrebnoi et al., 1997) differ by orders of magnitude from the corresponding mass spectral data obtained by these authors (compare the data in the third and fourth columns of Table 48).

Taking into account the above observations, we believe that the reliability of the measurements of saturated vapor pressures (Kapala et al., 2002; Khasanshin et al., 1999, 2001a,b; Kudin and Smirnov, 2003a,b; Kudin et al., 1997a,b, 2000, 2003a,b; Kuznetsov et al., 1997a, 1999; Pogrebnoi, 2004; Pogrebnoi et al., 1997, 2001) is not high, although the trend in changes in the enthalpy of reaction (18) along the lanthanide series obtained from these data is similar to the above trend obtained by processing the mass spectral data of the saturated vapor over trichlorides.

7.6 Mass spectra of EuCl₃ and Eu₂Cl₆

As already mentioned in the case of samarium and europium trihalides (Chervonnyi and Chervonnaya, 2007a,g), these compounds have low enthalpies of sublimation and tend to decompose at high temperatures. Hastie et al. (1968) made an effort to stabilize the trivalent europium state. These authors prepared a mixture of europium and lutetium trichlorides, which melt at different temperatures ($T_m = 894$ K for EuCl₃ and 1198 K for LuCl₃), and studied the composition of the vapor over this mixture by mass spectrometry. Data from the mass spectrum recorded at T = 960 K are presented in Table 49. At this temperature, the EuCl₃ melt is

TABLE 49 Mass spectrum of the saturated vapor over the EuCl₃-LuCl₃ system recorded at 960 K with E = 50 eV (Hastie et al., 1968)^{*a*}

R	R^+	RCl^+	RCl_2^+	RCl_3^+	$R_2Cl_5^+$	P _d ∕P _m (%)
Eu	-	1.2	1.5	3.6	0.1	1.08
Lu	70	35	100	26	11	3.17

^{*a*} The mass spectrum also evidences the presence of the EuLuCl₅⁺ ion with the intensity 0.28; P_d/P_m values are calculated by us.

embedded in solid lutetium trichloride. Based on the ionization efficiency curves recorded for the EuCl⁺ and EuCl⁺ ions, the authors assumed that these ions only partially originate from the EuCl₂ molecules (about 5% of the observed intensity). There main origin is the dissociative ionization of EuCl₃ molecules.

It is worth noting that in the mass spectrum of the vapor over this mixture, the Eu⁺ ion was not identified among the ions whose formation can be assigned to the ionization of Eu-containing molecules (Hastie et al., 1968). The Eu⁺ ion was not observed even upon the ionization of EuCl₂ molecules, despite the fact that, according to the mass spectrum of this compound at T = 1218 K (Hastie et al., 1968), the intensity of the Eu⁺ ions is about half as large as the maximum intensity of the EuCl⁺ ion.

Another point to be mentioned is that the EuCl_3^+ ion is the most abundant among the Eu-containing ions in the vapor over the $\text{EuCl}_3^ \text{LuCl}_3$ mixture, whereas RCl_2^+ is the most abundant for the other lanthanide trichlorides (Table 46). Further, EuCl_3^+ ions were not identified in the mass spectrum of the vapor over pure europium trichloride (Hastie et al., 1968); the spectrum was typical of the europium dichloride molecule, a fraction of EuCl_2^+ ions forming from EuCl_3 .

 $Eu_2Cl_5^+$ and $EuLuCl_5^+$ ions were also identified in the spectrum of the $EuCl_3$ -LuCl_3 mixture, which is evidence of the presence of Eu_2Cl_6 and the mixed dimer $EuLuCl_6$ in vapor. The emergence of the mixed dimer in a saturated vapor was also reported in studies of the mass spectra of vapor of binary systems of lanthanide trichlorides (Khasanshin et al., 1999; Pogrebnoi et al., 1999). Molecules of the RR'Cl_6 type were identified in the YbCl_3-LuCl_3, YbCl_3-DyCl_3, and TbCl_3-DyCl_3 systems. Their presence was deduced by the observation of the RR'Cl_5^+ ion.

The calculation by the third law of the enthalpy of reaction (18) from the mass spectra of LuCl₃ (Table 47) gives 232.0 kJ/mol, which is consistent with analogous thermodynamic parameters described by Eq. (19). Let us assume that under the experimental conditions used by Hastie et al. (1968), the LuCl₃ activity is close to unity. However, in this case, using the $P_{\rm m}({\rm LuCl}_3)$ pressure calculated with taking into account data from Chervonnyi and Chervonnaya (2007g) and the intensities of ion currents of this molecule from Table 49, one can determine the sensitivity constant of the mass spectrometer used by Hastie et al. (1968). Further calculation with the use of this sensitivity constant and the ion current corresponding to the EuCl₃ monomers and Eu₂Cl₆ dimers give $P_m(EuCl_3) = 1.46 \times 10^{-3}$ Pa and $P_d(\text{EuCl}_3) = 1.58 \times 10^{-5}$ Pa. In these calculations, the atomic ionization cross sections from Mann (1970) were used, and the molecular cross section for EuCl₃ was found using the additive scheme. In addition, the $EuCl^+$ and $EuCl_2^+$ ion currents were preliminarily decreased by 5%, which corresponded to the percentage of these ions originating from the EuCl₂ molecule.

Comparison of $P_{\rm m}({\rm EuCl_3})$ with the analogous value calculated from the data by Chervonnyi and Chervonnaya (2007g) shows that the partial pressure found from by Hastie et al. (1968) is considerably smaller. This seems to indicate that europium trichloride evaporates from a mixture in which the EuCl₃ activity is considerably lower than unity (our calculation gives ~1.44 × 10⁻⁴). In this case, the enthalpy of reaction (18) estimated from the above partial pressures $P_{\rm m}({\rm EuCl_3})$ and $P_{\rm d}({\rm EuCl_3})$ appears to be 247.7 kJ/mol; as a comparison, Eq. (19) gives $\Delta_{\rm r} H^{\circ}$ (298) = 212. 9 kJ/mol. However, this latter $\Delta_{\rm r} H^{\circ}$ (298) value means that the saturated vapor over europium trichloride should be virtually completely dimerized.

This conclusion is inconsistent with the trend in the change of the degree of association of the saturated vapor in the series of the compounds under consideration (Table 50). This inconsistency can be resolved by assuming that the EuCl₃ activity in the EuCl₃–LuCl₃ mixture is also close to unity. In this case, the calculation of the P_d/P_m ratio from the mass spectrum (Table 49) leads to a value which is more consistent with the above trend in the degree of association of saturated vapor.

Comparison of the enthalpies of reaction (18) recalculated by the second law at standard temperature from the corresponding measurements of ion currents as a function of temperature (Hastie et al., 1968) reveals the following specific features. For lutetium and europium trichlorides, $\Delta_r H^{\circ}(298, \text{II law})$ is equal to 205.9 ± 16.8 and 144.8 ± 25.8 kJ/mol, respectively. In the former case, the second-law calculation underestimates by ~ 30 kJ/mol the enthalpy of reaction as compared to the calculation by the third law. In the latter case, $\Delta_r H^{\circ}$ (298, II law) is lower by the same value than $\Delta_r H^{\circ}(298, \text{II law})$ determined from the mass spectral intensities (177.1 kJ/mol).

It is likely that such a low enthalpy of reaction (18) for europium trichloride is close to the actual value. If Hastie et al. (1968) did not make a technical error in recording the mass spectrum of the vapor over

RCl ₃	(P _d ∕P _m)100	RCl ₃	(<i>P</i> _d ∕ <i>P</i> _m)100
LaCl ₃	2.05	TbCl ₃	6.86
CeCl ₃	3.27	DyCl ₃	7.69
PrCl ₃	3.00	HoCl ₃	8.78
NdCl ₃	2.06	ErCl ₃	11.11
PmCl ₃	1.45	TmCl ₃	16.13
SmCl ₃	4.68	YbCl ₃	12.88
EuCl ₃	4.52	LuCl ₃	20.39
GdCl ₃	3.84	-	-

TABLE 50 Ratio P_d/P_m (in %) in the saturated vapor of lanthanide trichlorides at 1400 K

a EuCl₃–LuCl₃ mixture, the above specific features of the mass spectrum of europium trichloride are presumably associated with the anomalously small ionization cross section of this molecule. This argument was used by Hastie et al. (1968) to explain the presence of the EuCl₂⁺ ion formed upon ionization of EuCl₃ and the absence of the EuCl₃⁺ ion.

By technical error, we refer to the following circumstance. To extend the range of the measured ion current intensities, the electrometric amplifiers of a mass spectrometer allow for a jumpwise change in the input resistance (as a rule, by a factor of 10^k , where k = 2-4). As already mentioned, the activity was estimated at $\sim 10^{-4}$. If we assume that the intensities of Eu-containing ions were measured at an input resistance 10^4 times lower than the input resistance at which the intensities of Lu-containing ions were measured, the activity of EuCl₃ in the binary mixture is actually close to unity.

7.7 Standard thermodynamic characteristics of R₂Cl₆

The data on the enthalpy of reaction (18) obtained from the mass spectra of saturated vapor and described by Eq. (19) are the most reliable. The only exception is $\Delta_r H^{\circ}(298)$ for the reaction involving europium trichloride monomer and dimer. Substituting these results and the enthalpies of sublimation of monomers $\Delta_{sub}H^{\circ}(M, 298)$ from Chervonnyi and Chervonnaya (2007g) into Eq. (20) were calculated the enthalpies of sublimation of the dimeric compounds $\Delta_{sub}H^{\circ}(D, 298)$. It was also assumed that, for promethium trichloride, the enthalpy of reaction (18) can be estimated by Eq. (19).

In addition, the above $\Delta_r H^{\circ}(298)$ values and the enthalpies of atomization $\Delta_{at}H^{\circ}(\text{RCl}_3, 298)$ recommended by Chervonnyi and Chervonnaya (2007g) allowed us to calculate the same parameter for gaseous dimers of the lanthanide trichlorides. Selected values of the enthalpy of sublimation, the enthalpy of formation, and enthalpy of atomization are listed in Table 51. All calculations were performed by taking the needed parameters from IVTANTERMO (2004).

The errors on the enthalpies of reaction (18) recommended in this work were determined by taking into account the errors for all quantities involved in the equation for calculation by the third law (Chervonnyi, 1975). The major contribution consists in the errors for the determination of the ionization cross sections and thermodynamic functions. The error on the calculated reduced Gibbs energy of R_2Cl_6 molecules, ± 20 J/ (mol K) at 1000 K (Gorokhov and Osina, 2005), seems to be considerably overestimated, at least, for reaction (18) since this error is determined by the error of calculation of only the vibrational and rotational components of the reduced Gibbs energy. By the same reasoning, the error on the thermodynamic functions of RCl₃ molecules reported by Chervonnyi and

R	⊿ _{sub} H°(D, 298)	⊿ _f H°(298)	⊿ _{at} H°(298)	⊿ _f H°(0)	$\varDelta_{at} H^{\circ}(0)$
La	473.6	-1669.6	3257.412	-1670.583	3248.989
Ce	454.7	-1665.5	3227.460	-1666.575	3222.295
Pr	451.0	-1664.0	3103.438	-1666.600	3098.320
Nd	454.5	-1627.7	3009.770	-1630.800	3004.520
Pm	453.8	-1613.6	2859.738	-1615.335	2853.055
Sm	418.5	-1632.1	2771.106	-1629.601	2757.321
Eu	372.9	-1497.9	2578.086	-1501.642	2575.362
Gd	412.4	-1634.2	3159.034	-1631.512	3149.232
Tb	400.1	-1621.1	3121.024	-1620.382	3114.102
Dy	383.2	-1601.6	2899.916	-1602.545	2896.265
Ho	385.7	-1609.3	2937.494	-1610.983	2932.703
Er	381.4	-1609.6	2965.066	-1611.281	2959.001
Tm	376.9	-1615.5	2808.830	-1617.387	2803.107
Yb	384.8	-1533.6	2566.384	-1534.627	2558.347
Lu	379.5	-1588.9	3257.412	-1588.179	3161.899

TABLE 51 Enthalpies of sublimation of dimeric lanthanide trichlorides, enthalpies offormation, and enthalpies of atomization of the dimers under standard conditions,in kJ/mol^a

^a All primary (experimental) enthalpy values are given with an accuracy of 0.1 kJ/mol. Other values calculated from them have an accuracy of 0.001 kJ/mol, as accepted in IVTANTERMO (2004).

Chervonnaya (2004g) should be smaller. With respect to the above factors, the error on the determination of $\Delta_r H^{\circ}(298)$ does not exceed ± 6 kJ/mol.

For the enthalpy of atomization of R_2Cl_6 molecules, which is the algebraic sum of the enthalpy of atomization of RCl_3 and the enthalpy of reaction (18), the error, determined as the square root of the sum of the squares of the errors of the summands (Gurvich et al., 1978–1984), does not exceed ± 12 kJ/mol.

Dependences of the R_2Cl_6 saturated vapor pressure over lanthanide trichlorides have been described by Kudin and Vorob'ev (2005). This work mainly reproduces the earlier results (Pogrebnoi, 2004), with exception for the data on Gd_2Cl_6 , Dy_2Cl_6 , and Lu_2Cl_6 , which are somewhat different. Inasmuch as the original experimental data (Pogrebnoi, 2004) are comprehensively discussed in the present work, we only mention the results obtained by Kudin and Vorob'ev (2005). Indeed, it is of interest to note that these authors failed to identify the EuCl₃ and/or Eu₂Cl₆ molecules when reproducing the experimental conditions used by Hastie et al. (1968) in studying the evaporation of the EuCl₃–LuCl₃ mixture. We have no reasons to doubt the correctness of the results reported by Hastie et al. (1968), especially that the rather high reliability of high-temperature measurements conducted in Margrave's laboratory is well known.

8. ENTHALPIES OF FORMATION OF CRYSTALLINE LANTHANIDE DICHLORIDES

Systemic analysis of the enthalpies of formation at the standard temperature for crystalline lanthanide dichlorides $\Delta_f H^{\circ}(\text{RCl}_2, \text{ cr}, 0)$ [or $\Delta_f H^{\circ}(\text{RCl}_2,$ cr, 298)] is important not only for revealing reliable values for use in thermodynamic calculations but also for ascertaining the enthalpies of formation for compounds hitherto unsynthesized. Despite the fact that the possibility to form compounds in the R²⁺ state has been established almost for the entire lanthanide series (Mikheev et al., 1992), dichlorides have not yet been synthesized for lanthanum, cerium, praseodymium, promethium, gadolinium, terbium, erbium, and lutetium. The reasons for this failure were investigated repeatedly, for example, by Johnson (1969) or Kim and Oishi (1979), through analyzing the thermodynamic stability of RCl₂ as revealed by the enthalpy of disproportionation at 298 K of the following reaction:

$$RCl_2(cr) = \frac{2}{3}RCl_3(cr) + \frac{1}{3}R(cr)$$
 (22)

which was calculated from the enthalpies of formation $\Delta_{f}H^{\circ}(298)$ of the compounds involved in the equilibrium.

Some of the data required for these calculations were taken from handbooks or original works. Most of them were, however, estimated using approximate methods. At the moments when these calculations were performed, the enthalpies of formation of lanthanide dichlorides were the least known parameters; they were estimated using various methods (Johnson, 1969; Kim and Oishi, 1979).

Johnson (1969) calculated $\Delta_f H^{\circ}(\text{RCl}_2, \text{ cr, 298})$ using the Born–Haber cycle, with the RCl₂ lattice energies found from Kapustinskii's equation. Kim and Oishi (1979) used, for the same purpose, the transition energies between the $4f^n d^1 6s^2$ and $4f^{n+1} d^0 6s^2$ configurations in a lanthanide atom upon the formation of an RCl₂ molecule. In both studies, the calculations concerned the lanthanide chlorides from lanthanum through ytterbium and, despite the different approaches used, their results are consistent.

Indeed, when Johnson (1969) published his paper, four experimental values of $\Delta_{\rm f} H^{\circ}({\rm RCl}_2, {\rm cr}, 298)$ were known, for neodymium, samarium, europium, and ytterbium dichlorides. One decade later, Kim and Oishi (1979) could compare their estimates with the experimental values for six dichlorides, dysprosium and thulium dichlorides data having been added in the meantime.

However, new experimental determinations of $\Delta_f H^{\circ}(\text{RCl}_2, \text{ cr, } 298)$ performed more recently by Goryushkin et al. (Goryushkin, 1994; Goryushkin et al., 1989a,b, 1990a,c, 1992b, 1994) and analyzed by Laptev

(1996) by means of the procedure used by Johnson (1969) cast doubt on the reliability of the final results.

First, a significant discrepancy exists in the $\Delta_{\rm f} H^{\circ}$ (EuCl₂, cr, 298) values: Goryushkin (1994) reported -833.2 ± 1.2 kJ/mol, while Laptev (1996) found -822.7 ± 0.7 kJ/mol. Based on the analysis of the thermodynamic parameters of gaseous europium chlorides and on the saturated vapor pressures of europium dichloride, we think that $\Delta_{\rm f} H^{\circ}$ (EuCl₂, cr, 298) = - 824. 2 ± 7. 1 kJ/mol, proposed by Morss and Haug (1973), is the most suitable value (see Chervonnyi and Chervonnaya, 2004a, 2005b).

Second, since the currently used values (IVTANTERMO, 2004) can differ from those considered previously, the experimental measurements of the enthalpies of formation (Goryushkin, 1994; Goryushkin et al., 1989a,b, 1990a,c, 1992b, 1994; Laptev, 1996), which were performed in solid galvanic cells with a unipolar intermediate electrolyte, can be corrected by means of new thermodynamic functions for the condensed state of both the lanthanide dichlorides and the rare-earth and alkaline-earth atoms (as well as alkaline-earth dichlorides). In particular, our recalculation (Chervonnyi and Chervonnaya, 2004f) of the enthalpy of formation for YbCl₂ resulted in $\Delta_f H^{\circ}$ (YbCl₂, cr, 298) = -782.0 ± 1.5 kJ/mol instead of -780.8 ± 1.5 kJ/mol reported by Goryushkin et al. (1994).

Third, we not only refined the thermodynamic properties of individual compounds, including lanthanide trichlorides for which a critical review of their enthalpies of formation was published in 2001 (Cordfunke and Konings, 2001a), but also the atomic ionization energies (IEs) (CRC Handbook, 2000–2001; NIST Ground Levels) and the crystalline ionic radii (Shannon, 1976), that is, the ancillary characteristics dealt with by Johnson (1969) and Kim and Oishi (1979). In addition, when using advanced schemes (Johnson, 1969; Kim and Oishi, 1979), one should use the characteristics referred to one temperature, best of all, 0 K. Currently, experimentally determined enthalpies $H^{\circ}(298) - H^{\circ}(0)$ exist for the entire lanthanide series (Gavrichev et al., 1987a,b; Tolmach et al., 1986, 1987a,b), which are required for the enthalpies of formation to be converted from 298 to 0 K.

Fourth, all of the lanthanide dichlorides for which the enthalpies of formation were determined have not been synthesized. Some samples contained unreacted metal. In addition, the e.m.f., required to derive the enthalpy of formation, was measured at relatively high temperatures (600–800 K), at which decomposition can be noticeable. These are possible reasons for additional uncertainties on $\Delta_f H^{\circ}(\text{RCl}_2, \text{ cr, } 298)$.

Therefore, in this section, we calculated $\Delta_f H^{\circ}(\text{RCl}_2, \text{ cr}, 0)$ using a combination of the schemes (Johnson, 1969; Kim and Oishi, 1979) to find consistent values among the experimental data and to estimate lacking values for the RCl₂ with R = La, Ce, Pr, Pm, Gd, Tb, and Lu.

8.1 Energies of the $4f^{n}5d^{1}6s^{2} \rightarrow 4f^{n+1}5d^{0}6s^{2}$ transitions for lanthanide atoms, calculation of $\Delta_{f}H^{\circ}(\text{RCl}_{2}, \text{ cr, } 0)$

The calculation scheme for the enthalpies of formation of lanthanide dihalides proposed by Kim and Oishi (1979) is based on the assumption that the formation of these compounds, except for europium and ytterbium, is accompanied by an electronic transition $4f^{n}5d^{1}6s^{2} \rightarrow 4f^{n+1}5d^{0}6s^{2}$ in the lanthanide atom. This results in the observation of an irregularity in the variation of the thermodynamic parameters, including the enthalpies of formation, as a function of the lanthanide atomic number.

This assumption was made from the irregular trend of the enthalpy of formation $\Delta_f H^{\circ}(R, 298)$, which is numerically equal to the enthalpy of sublimation $\Delta_{sub}H^{\circ}(R, 298)$ for lanthanide atoms as shown by Brewer (1971). This irregularity is attributed to the different electronic configurations of the atoms in the condensed and gas phases. Namely, almost all lanthanides, when sublimed, experience the aforementioned change in the electronic configuration. Exceptions are lanthanum, cerium, and gadolinium, which retain their tervalent configurations (d¹s²) in the gas, and ytterbium and europium, which have divalent configurations (d⁰s²) in both the condensed and gas phases.

We also took into account the results of Johnson's thermochemical analysis (Johnson, 1969), in which the energy of a chemical process with the retention of the number of 4f electrons varies smoothly in the lanthanide series.

From this, when analyzing the plot of the enthalpy of formation of an element as a function of its atomic number (Figure 26), we assigned the difference between the $\Delta_f H^{\circ}(M, 298)$ curve and the value taken from the monotonous curve which connects the points representing the enthalpies of formation of ytterbium, europium, and barium (Figure 26), to the enthalpy of a valence transition of the lanthanide from the tervalent to the divalent state: $\Delta_{VC}H^{\circ}_{298}(III \rightarrow II)$. The enthalpy of formation of atomic barium was chosen to be an additional reference, since the barium electronic configuration may be regarded as $4f^{0}5d^{0}6s^{2}$ for both gaseous and condensed phases. This approximation is suitable for all of the members of the lanthanide series except for lanthanum, cerium, and gadolinium. For these exceptions, we had to increase the difference by adding the energy of the electronic transition $4f^{n}d^{1}6s^{2} \rightarrow 4f^{n+1}d^{0}6s^{2}$, a value reported for instance by Martin et al. (1978).

In order to obtain the enthalpy of formation for the dihalide series, the next calculation step was to sum the $\Delta_{VC}H^{\circ}(III \rightarrow II, 298)$ enthalpies with the value obtained from the monotonous curve that connects the enthalpies of formation for barium, europium, and ytterbium dihalides (Figure 27). It is noteworthy that Johansson (1979) proposed this calculation scheme for the enthalpy of the valence transition of the lanthanides at the same time as Kim and Oishi (1979) did.



FIGURE 26 Enthalpies of formation for barium and the lanthanides. Reproduced from Chervonnyi and Chervonnaya (2005c) with permission from Pleiades Publishing, Ltd.



FIGURE 27 Enthalpies of formation for barium and lanthanide dichlorides. Reproduced from Chervonnyi and Chervonnaya (2005c) with permission from Pleiades Publishing, Ltd.

From the described calculation procedure, it is clear that the estimation accuracy, as well as the efficiency of the scheme, is significantly controlled by the care taken in choosing the references. In our calculations, we used $\Delta_f H^{\circ}(R, 0)$, $\Delta_f H^{\circ}(Ba, 0)$, and $\Delta_f H^{\circ}(BaCl_2, cr, 0)$ in accordance with the recommendations in IVTANTERMO (2004). The values of $\Delta_f H^{\circ}(EuCl_2, cr, 0) = -822.635 \text{ kJ/mol}$ and $\Delta_f H^{\circ}(YbCl_2, cr, 0) = -782.489 \text{ kJ/mol}$ are the recommended $\Delta_f H^{\circ}(RCl_2, cr, 298)$ values from Chervonnyi and Chervonnaya (2004a, f, 2005b) converted to 0 K. The conversion was performed using the following relationship:

$$\begin{split} \Delta_{\rm f} H^{\circ}({\rm RCl}_2,{\rm cr},0) &= \Delta_{\rm f} H^{\circ}({\rm RCl}_2,{\rm cr},298) + [H^{\circ}(298) - H^{\circ}(0)]_{\rm R} \\ &+ [H^{\circ}(298) - H^{\circ}(0)]_{\rm Cl_2} - [H^{\circ}(298) - H^{\circ}(0)]_{\rm RCl_2}. \end{split}$$

The required enthalpy values were taken from the database (IVTANTERMO, 2004) and from Chervonnyi and Chervonnaya (2008a).

The reference enthalpies of formation for barium, europium, and ytterbium plotted as a function of the atomic number (Ba, La–Lu; n = 1–16) and for the dichlorides of these elements (see Table 52) were fitted to smooth curves by means of a second-order polynomial.

The enthalpy of the valence transition may be presented as follows: for Pr–Sm and Tb–Tm,

$$\Delta_{\rm VC}H^{\circ}({\rm III} \to {\rm II}, 0) = \varDelta_{\rm f}H^{\circ}({\rm R}, 0) - (185.40367 + 0.48572n - 0.17640n^2); (23)$$

for La, Ce, and Gd,

$$\Delta_{\rm VC} H^{\circ}({\rm III} \to {\rm II}, 0) = \varDelta_{\rm f} H^{\circ}({\rm R}, 0) - (185.40367 + 0.48572n - 0.17640n^2) + E(4f^n d^1 6s^2 \to 4f^{n+-1} d^0 6s^2).$$
(24)

The enthalpies of formation of the dichloride for the series La–Sm and Gd–Tm are, accordingly,

$$\Delta_{\rm f} H^{\circ} ({\rm RCl}_2, {\rm cr}, 0) = (-859.979 + 4.09886n + 0.07114n^2) + \Delta_{\rm VC} H^{\circ} ({\rm III} \to {\rm II}, 0)$$
(25)

In accordance with Kim and Oishi's scheme (Kim and Oishi, 1979) and with Brewer's recommendations (Brewer, 1971), we included the promotion energies of the electronic configuration $E(4f^n \rightarrow 4f^{n+1})$ into the enthalpies of valence transition for lanthanum, cerium, and gadolinium (see Eq. (25)). These energies are 1.884167 eV for La, 0.590502 eV for Ce, and 1.357281 eV for Gd according to Martin et al. (1978).

The calculations for lutetium dichloride were not performed with the above scheme, as in Johnson's evaluation (Johnson, 1969). Evidently, with the 4f shell completely filled, the promotion scheme to the divalent configuration for atomic lutetium should differ from the scheme above.

N	м	$\Delta_{\rm f} {\cal H}^{\circ \circ}$ (M, g, 0) [°]	$\Delta_{ m VC} H^{\circ}(m III ightarrow m II, 0)$	$\Delta_{ m f} { m H}^{\circ}({ m MCl}_2,{ m cr}$, 0)			
1	Ba	185.713 ^b	0	-855.809 ^c	-859.2^{d}	-859.2^{e}	_	-
2	La	430.343	426.463	-425.034^{f}	-501.900^{8}	_	-	_
3	Ce	419.000	290.697	-556.345^{f}	-554.807^{8}	_	-	_
4	Pr	357.000	172.476	-669.969 ^f	_	_	-	_
5	Nd	328.000	144.578	-693.128^{f}	-694.8^{d}	-707.1 ± 4.2^{e}	-700.0 ± 1.2^{h}	_
6	Pm	260.000	78.032	-754.793 ^f	_	_	-	_
7	Sm	205.000	24.840	-802.961^{f}	-816.8^{d}	-803.9^{e}	-799.3 ± 2.8^{i}	-803.3 ± 0.8^{j}
8	Eu	178.000 ^b	0	-822.635^{c}	-805.9^{d}	-822.8 ± 5.9^{e}	-831.6 ± 1.2^{k}	-821.0 ± 0.7^{j}
9	Gd	400.000	355.473	-461.854^{f}	-488.280^{8}	_	-	_
10	Tb	388.000	215.379	-596.497^{f}	_	_	-	_
11	Dy	288.000	118.598	-687.686 ^f	_	-692.2^{e}	-675.6 ± 2.5^{l}	_
12	Ho	302.000	136.169	-664.380^{f}	_	_	-660.2 ± 6.9^{m}	_
13	Er	315.000	153.094	-641.577^{f}	_	_	-	_
14	Tm	234.000	76.371	-712.281^{f}	_	-709.7 ± 4.2^{e}	-713.4 ± 2.9^{n}	_
15	Yb	153.000 ^b	0	-782.489^{c}	-799.6 ^d	-800.1^{e}	$-781.3 \pm 1.5^{\circ}$	$-780.5 \pm 1.5^{\prime}$
16	Lu	428.000	-	-426.745^{f}	-431.872^{8}	-	-	-

TABLE 52 Enthalpies of formation for crystalline barium, and lanthanide dichlorides and for their metal

^{*a*} IVTANTERMO (2004). ^{*b*} Reference values for calculation of Δ_{VC}H^o(III → II, 0). ^{*c*} Reference values for Δ₄H^o(MCl₂, cr, 0). ^{*d*} Experimental data from Johnson (1969). ^{*e*} Experimental data from Kim and Oishi (1979). ^{*f*} Our calculations using Kim and Oishi's method (Kim and Oishi, 1979). ^{*f*} Our calculations from the Born–Haber cycle. ^{*h*} Recalculated data from Goryushkin et al. (1990c). ^{*i*} Recalculated data from Goryushkin et al. (1992b). ^{*i*} Recalculated data from Goryushkin (1994). ^{*k*} Recalculated data from Goryushkin et al. (1989b). ^{*m*} Recalculated data from Goryushkin et al. (1990a). ^{*m*} Recalculated data from Goryushkin et al. (1990a). ^{*n*} Recalculated data from Goryushkin et al. (1989a). ^{*o*} Recalculated data from Goryushkin et al. (1994).

In addition, the final results in the calculation sequence in question are affected by the choice of the enthalpies of formation of the references.

We used the Born–Haber cycle to estimate $\Delta_{f}H^{\circ}(LuCl_{2}, cr, 0)$ and to verify the results for consistence.

8.2 Calculation of the enthalpy of formation using the Born-Haber cycle

In accordance with this cycle,

$$-\begin{bmatrix} \mathsf{R}(\mathsf{cr}) & \xrightarrow{\Delta_{l}H^{\circ}(\mathsf{R},0)} & \mathsf{R}(\mathsf{g}) & \xrightarrow{\mathsf{IE}_{1}+\mathsf{IE}_{2}} & \mathsf{R}^{2+}(\mathsf{g}) \\ \\ \mathsf{Cl}_{2} & \xrightarrow{\Delta_{\mathsf{at}}H^{\circ}(\mathsf{Cl}_{2},0)} & \mathsf{2Cl} & \xrightarrow{\mathsf{2EA}} & \mathsf{2Cl}^{-} \end{bmatrix} \\ \xrightarrow{\Delta_{t}H^{\circ}(\mathsf{RCl}_{2},\operatorname{cr},0)} & \mathsf{RCl}_{2}(\mathsf{cr}) & \longleftarrow^{U^{\circ}} \end{bmatrix}$$

the lattice energy can be found from:

$$U^{\circ} = -\varDelta_{f}H^{\circ}(RCl_{2}, cr, 0) + \Delta_{f}^{\circ}(R, 0) + (IE_{1} + IE_{2}) + \varDelta_{at}H^{\circ}(Cl_{2}, 0) + 2EA(Cl)$$
(26)

Here, U° is the lattice energy, which is actually the enthalpy of formation of the crystal lattice from ions in the gaseous state; IE₁ and IE₂ are the first and second IEs of the lanthanide; $\Delta_{at}H^{\circ}(Cl_2, 0)$ is the atomization energy of Cl_2 ; and EA(Cl) is the electron affinity of chlorine at T = 0.

The calculations of this quantity by means of Eq. (26) using the enthalpies of formation chosen from experimental data (for EuCl₂ and YbCl₂) and those found from Eqs. (23) to (25) for the other lanthanide dichlorides allow us to use U° to subsequently calculate the crystalline radii of the R²⁺ cations. Kapustinskii's equation seems to be quite adequate for this purpose:

$$U^{\rm o} = \frac{1240kz_{\rm R}z_{\rm Cl}}{r^+ + r^-} \left(1 - \frac{0.345}{r^+ + r^-}\right) \tag{27}$$

where r^+ and r^- are the ionic radii (Å) of \mathbb{R}^{2+} and \mathbb{Cl}^- in the crystal lattice, respectively, k is the number of atoms in the molecule, and $z_{\mathbb{R}}$ and $z_{\mathbb{Cl}}$ are the atomic charges.

The positive point is that Kapustinskii's equation was derived on the assumption that any structural type can hypothetically be transformed into the NaCl lattice (CN = 6) without change in the lattice energy. Therefore, in spite of the different crystal structures of the lanthanide dichlorides (Astakhova and Goryushkin, 1992; Astakhova et al., 1977, 1991a,b; Goryushkin, 1996; Goryushkin et al., 1990d; Laptev and Astakhova, 1981; Laptev et al., 1976a; Meyer, 1988; Poshevneva, 1985), the use of this equation should yield a smooth curve of the crystalline R^{2+} ion radii as a function of the lanthanide atomic number, in fact, reflecting the lanthanide contraction.

N	М	IE1 ^a	IE ₂ ^b	U° ^c	r ^{+d}	r ^{+e}	U° ^f
2	La	5.5770	11.059	2002.3	1.430	1.294	2079.2
3	Ce	5.5387	10.851	2098.5	1.261	1.264	2097.0
4	Pr	5.4640	10.551	2114.0	1.235	1.235	2114.1
5	Nd	5.5250	10.727	2131.0	1.207	1.208	2130.7
6	Pm	5.5820	10.903	2147.1	1.181	1.182	2146.7
7	Sm	5.6437	11.069	2162.3	1.157	1.158	2162.0
8	Eu	5.6704	11.245	2174.6	1.138	1.135	2176.6
9	Gd	6.1502	12.095	2164.1	1.154	1.113	2190.5
10	Tb	5.8639	11.525	2204.1	1.092	1.093	2203.6
11	Dy	5.9390	11.670	2216.5	1.074	1.074	2216.0
12	Ho	6.0216	11.805	2228.3	1.056	1.057	2227.6
13	Er	6.1078	11.929	2238.7	1.040	1.041	2238.3
14	Tm	6.18431	12.054	2247.8	1.027	1.027	2248.2
15	Yb	6.25416	12.188	2256.7	1.014	1.013	2257.2
16	Lu	5.42585	13.888	2260.1	1.009	1.002	2265.2

TABLE 53 Ionization energies (eV), lattice energies (kJ/mol), and ionic radii (Å) for
lanthanide dichlorides

^{*a*} Taken from NIST Ground Levels.

^b Taken from CRC Handbook (2000–2001).

^c Calculated using the Born–Haber cycle from the $\Delta_t H^{\circ}$ (MCl₂, cr, 0) found with the use of Kim and Oishi's method (Kim and Oishi, 1979).

^d Calculated using Kapustinskii's equation from the lattice energies displayed in the preceding column of the table.

^e Calculated from the polynomial dependence of the radii as a function of the lanthanide number.

^f Found using Kapustinskii's equation from the radii displayed in the preceding column of the table.

Indeed, if we use refined values of the first and second IEs of lanthanide atoms from the NIST website or from the CRC Handbook (2000–2001) (cf. Table 53) in calculating the lattice energies and if we take the enthalpies of formation listed in Table 52, the enthalpy of atomization of molecular chlorine ($\Delta_{at}H^{\circ}(Cl_2, 0) = 239.240 \text{ kJ/mol}$) and the electron affinity of atomic chlorine EA(Cl) = -348.700 kJ/mol from IVTANTERMO (2004), then the resulting U° will lead to the R²⁺ crystal-line radii that are described with a very high accuracy by the following second-order polynomial, except for La²⁺, Gd²⁺, and Ce²⁺ radii:

$$r^{+} = 1.35769 - 0.03350n + 7.03249 \times 10^{-4} n^{2}$$
⁽²⁸⁾

where *n* is the number of the element in the $La^{2+}-Lu^{2+}$ series (*n* = 2–16).

In the calculations by means of Kapustinskii's equation, we used a value of 1.81 Å for the crystalline radius of the Cl⁻ ion in accordance with Shannon's data (Shannon, 1976), in which crystalline radii are given for several R^{2+} ions (Sm²⁺, Eu²⁺, Tm²⁺, and Yb²⁺) in lattices with various CNs. The radii for CN = 6 are displayed in Figure 28, together with the



FIGURE 28 Crystalline radii for the R^{2+} ions: \bigcirc), calculated using the Born–Haber cycle and Kapustinskii's equation from the enthalpies of formation found with the use of Kim and Oishi's scheme (Kim and Oishi, 1979); \blacktriangle , Shannon's data (Shannon, 1976). The solid curve connects the values calculated from the fit of polynomial (28). Reproduced from Chervonnyi and Chervonnaya (2005c) with permission from Pleiades Publishing, Ltd.

values calculated from Kapustinskii's equation. The fit curve (Eq. (28)) is shown in the same figure.

It follows from Figure 28 that the crystalline radii that we calculated for the Sm^{2+} , Tm^{2+} , and Yb^{2+} ions correlate well with Shannon's data (Shannon, 1976). Poorer correlation is observed for the Eu²⁺ ion. Two facts are, however, worth noting. First, Shannon (1976) reported the results obtained by comparison methods from the structural parameters of oxide and fluoride crystals. Second, the Eu²⁺ ion radius versus CN dependence implies that the divalent europium ion radius in a crystal with CN = 6 is 1.15 Å rather than 1.17 Å. The thus corrected Shannon's data (Shannon, 1976) correlate better with our values for the Eu²⁺ ion radius.

It is believed that known relationships, including Kapustinskii's equation, yield approximate values of the lattice energy. As a rule, these values do not converge with the results of Born–Haber calculations. The term "thermochemical radius" appeared, meaning the radius that is derived from the lattice energy found on the basis of thermochemical data.

In sample calculations, we estimated the radii for alkaline-earth dichlorides, which are compared in Table 54 with the smoothed data from Shannon (1976). The calculation method was similar to that described above for finding bivalent lanthanide radii. These calculations were performed with the goal of elucidating the weaknesses of the

м	$\Delta_{\rm f} H^{\circ} ({\sf M}, 0)^{a}$	$\Delta_{\rm f} {\rm H^{\circ}({ m MCl}_2, cr, 0)}^a$	IE1 ^b	IE ₂ ^c	$U^{\circ}(MCl_2)^d$	r ^{+e}	r ^{+f}	δ_r^{g}	
	(kJ∕mol)						(Å)		
Са	177.339	-796.183	589.8	1145.4	2250.562	1.02302	1.023	2×10^{-5}	
Sr	160.873	-833.479	549.5	1064.2	2149.892	1.17686	1.178	1×10^{-3}	
Ba	185.713	-855.809	502.8	965.2	2051.362	1.3417	1.343	1×10^{-3}	

TABLE 54Comparison of the thermochemical and crystalline radii of Ca^{2+} , Sr^{2+} , and Ba^{2+} in alkaline-earth dichlorides

^a IVTANTERMO (2004).
 ^b NIST Ground Levels.
 ^c CRC Handbook (2000–2001).
 ^d Our calculations using the Born–Haber cycle.
 ^e Our calculations using Kapustinskii's equation.
 ^f Polynomially smoothed Shannon's data (Shannon, 1976).
 ^g Difference between the crystalline radii from the two preceding columns of the table.
scheme and referred to compounds with similar properties. According to the data listed in Table 54, the discrepancies between the thermochemical and crystalline radii for these compounds are, however, very small.

Thanks to the observed practical match of the thermochemical and crystalline radii for alkaline-earth dichlorides, we think that the departure of the La^{2+} and Gd^{2+} crystalline ion radii from the smoothed curve in Figure 28 is due to incorrect calculation of the enthalpies of formation of the dichlorides: the promotion energy to the bivalent state for these lanthanides is inadequately taken into account in the framework of the scheme in question (Kim and Oishi, 1979). Therefore, it is reasonable to carry out inverse calculations. Namely, the crystalline radii of these ions, as well as of Ce^{2+} and Lu^{2+} ions, are estimated from Eq. (28); next, the lattice energies of the dichlorides of these ions are recalculated to be used in finding the enthalpies of formation of these compounds in crystals.

The calculations showed that for the radii found from Eq. (28) $(r_{La^{2+}} = 1.294, r_{Ce^{2+}} = 1.264, r_{Gd^{2+}} = 1.113, r_{Lu^{2+}} = 1.002 \text{ Å})$, the lattice energies (in kJ/mol) are 2079.2 (LaCl₂), 2097.0 (CeCl₂), 2190.5 (GdCl₂), and 2265.2 (LuCl₂). The last series leads to the following values for the enthalpies of formation calculated with Eq. (26), $\Delta_{f}H^{\circ}$ (MCl₂, cr, 0) (in kJ/mol) : – 501.900 (LaCl₂), – 554.807 (CeCl₂), – 488.280 (GdCl₂), and – 431.872 (LuCl₂).

To obtain the same values with Kim and Oishi's scheme (Kim and Oishi, 1979), we need to know the promotion energies of the valence configuration of a lanthanide, which correspond to Brewer's recommendations (Brewer, 1971) only for cerium. The energy of the $4f^n \rightarrow 4f^{n+1}$ transition from the ground state of atomic cerium to the excited state ${}^{3}H_{4}$ coincides with the calculated value of the promotion energy from Martin et al. (1978). In other cases, the promotion energies are close to the energies of the excited states formed through transitions $6s \rightarrow 5d$ (La and Gd) and $5d \rightarrow 6p$ (Lu). This follows from the comparison of the energies of the excited states (Martin et al., 1978).

When we calculated the enthalpies of formation for crystalline lanthanide dichlorides, the references used were the $\Delta_f H^\circ$ (EuCl₂, cr, 0) and $\Delta_f H^\circ$ (YbCl₂, cr, 0) recommended on the basis of previous analysis (Chervonnyi and Chervonnaya, 2004a,f, 2005b). In fact, they differ little (within the estimated error) from the experimental results obtained by Laptev (1996) for EuCl₂ and by Goryushkin et al. (1994) for YbCl₂.

In our previous work (Chervonnyi and Chervonnaya, 2004e) that concerned the thermodynamic properties of SmCl₂, we used $\Delta_{\rm f} H^{\circ}$ (SmCl₂, cr, 0) = -802.8 ± 2.2 kJ/mol, which was calculated from the data of Morss (1976). Comparing this value with the result obtained by means of the scheme above (see Table 52), we see that the discrepancy is as little as 0.2 kJ/mol. From Laptev's data (Laptev, 1996), it follows that the use of the experimentally determined heat of formation for this

compound will lead to $\Delta_{\rm f} H^{\circ}({\rm SmCl}_2, {\rm cr}, 0) = -803.3 \pm 0.8 \text{ kJ/mol}$. The use of the data of Goryushkin et al. (1992b) results in a somewhat poorer agreement for the same parameter $\Delta_{\rm f} H^{\circ}({\rm SmCl}_2, {\rm cr}, 0) = -799.3 \pm 2.8 \text{ kJ/mol}$. However, as for YbCl₂, this might be due to an overestimate by ca. 1–1.5 kJ/mol (Chervonnyi and Chervonnaya, 2004f).

Noteworthy is the minor discrepancy (1.2 kJ/mol) between the enthalpy of formation for crystalline thulium dichloride that we calculated by the method above and the experimentally derived enthalpy from Goryushkin et al. (1989a).

Such a close agreement between the calculated and experimental enthalpies of formation for samarium, europium, thulium, and ytterbium dichlorides allows us to claim that the calculation scheme used in the framework of this study leads to reliable results provided that the reference values are chosen adequately.

For the enthalpies of formation of neodymium, dysprosium, and holmium dichlorides, the calculated and experimental values are less consistent (see Table 52). However, this does not seem surprising if we recall that the stoichiometries of these compounds are not so easy to control, as opposed to the aforementioned compounds.

The enthalpy of reaction (22) at 298.15 K has been calculated by Johnson (1969) and Kim and Oishi (1979) to predict the stability of the lanthanide dichlorides: the possibility for this reaction to occur was judged from the enthalpy value. If we use the enthalpies of formation of the atomic lanthanides from IVTANTERMO (2004) (see Table 52), of the lanthanide trichlorides from Table 44, and of the lanthanide dichlorides from our calculations, the resulting enthalpy of reaction (22) has a higher positive value (see Figure 29) for all members of the series compared to the the earlier data (Johnson, 1969; Kim and Oishi, 1979).

According to our calculations, a negative enthalpy value is retained for reaction (22) only with La, Ce, Gd, or Lu. Therefore, only these elements have unstable dichlorides in the condensed state.

Nonetheless, the scope of the lanthanides for which dichlorides have no yet been prepared is far wider. Reasons for the failed syntheses are considered in several papers (Meyer, 1988; Meyer and Meyer, 1992; Mikheev et al., 1992). Likely, the stability of these compounds can be more reliably ascertained on the basis of the standard oxidation potentials of R^{3+}/R^{2+} pairs $E^{\circ}(R^{3+}/R^{2+})$ in accordance with

$$\Delta G^{\circ} = -FE^{\circ} \left(\mathbf{R}^{3+} / \mathbf{R}^{2+} \right),$$

Here, *F* is the Faraday constant, F = 96,485.3415 C/mol.

Experimental $E^{\circ}(\mathbb{R}^{3+}/\mathbb{R}^{2+})$ values in aqueous solutions for the entire series (without lutetium) are found in Mikheev et al. (1992).

Analyzing these data, we see that the $E^{\circ}(\mathbb{R}^{3+}/\mathbb{R}^{2+})$ values for the lanthanide (La, Ce, Pr, Gd, Tb, Dy) series are close to -3 V, that is, to



FIGURE 29 Enthalpy of disproportionation reaction (22) as a function of the number of the lanthanide in the series: \Box , data from Johnson (1969); \bigcirc , data from Kim and Oishi (1979); and Δ , our calculations. Reproduced from Chervonnyi and Chervonnaya (2005c) with permission from Pleiades Publishing, Ltd.

the value of the oxidative potential reached for lithium (the strongest reducing agent known hitherto). Therefore, it is extremely difficult to obtain compounds in which these lanthanides are divalent.

Pogrebnoi and Kudin (2003b), with reference to the study of Johnson (1969), see an analogy in the properties of alkaline-earth dichlorides and some lanthanide dichlorides, namely, they consider the similarity of the CaCl₂–SrCl₂–BaCl₂ and SmCl₂–EuCl₂–YbCl₂ series. Comparing the enthalpies of formation of these compounds pairwise, Pogrebnoi and Kudin (2003b) recommend the following values as being reliable: $\Delta_f H^{\circ}$ (RCl₂, cr, 298): -803.1 ± 2.7 for SmCl₂ (Goryushkin and Laptev, 1985), -824.4 ± 0.9 for EuCl₂ (Morss and Haug, 1973), and -831.4 ± 3.0 for YbCl₂ (Laptev and Kiseleva, 1994) kJ/mol. Of the three values mentioned in the work of Pogrebnoi and Kudin (2003b), two, for SmCl₂ and EuCl₂, are close to the values recommended on the basis of the results obtained in the present study and have been already considered (Chervonnyi and Chervonnaya, 2004a,f, 2005b). The third value differs by ca. 50 kJ/mol.

The choice of the value for YbCl₂ seems unjustified. First, the value of -831.4 ± 3.0 kJ/mol does not match the calculation scheme (Kim and Oishi, 1979) or the Born–Haber cycle and Kapustinskii's equation. Later, Laptev (1996) did not recommend this value for use as a reliably measured quantity.

Second, the analogy mentioned in Pogrebnoi and Kudin (2003b) in the thermodynamic parameters for the two classes of compounds, although already stated by Kim and Oishi (1979), was confirmed in the framework of the method used here. Hariharan and Eick (1972) evaluated the characteristics required for the calculation of EuCl₂ thermodynamic functions through comparing them with the data for calcium, strontium, and barium dichlorides and did not mention whether a similarity in the properties of YbCl₂ and BaCl₂ is possible. Hariharan et al. (1972) in their other study compared YbCl₂ properties not with BaCl₂ but with CaCl₂, which was considered as isostructural to ytterbium dichloride. Thus, the CaCl₂–SrCl₂–BaCl₂ and SmCl₂–EuCl₂–YbCl₂ analogies are not so clear as they were claimed (Pogrebnoi and Kudin, 2003b).

Analysis of the enthalpies of formation of crystalline lanthanide dichlorides not only provided an opportunity to obtain the characteristics (Table 55), necessary to describe the thermodynamic properties of this class of compounds, but mainly shows how difficult is the task of describing their thermodynamic functions. Obviously, for RCl₂(cr) experimental data on the measurement of heat capacity, temperatures and enthalpies of phase transitions are very incomplete and contradictory. This will be shown and discussed in the next section.

$\Delta_{\rm f} H^{\circ} ({\rm RCl}_2, {\rm cr}, 0)$	$\Delta_{\rm f} H^{\circ} ({ m RCl}_2, { m cr}, 298)$
-501.900	-501.732
-554.807	-555.973
-669.969	-669.637
-693.128	-692.898
-754.793	-754.971
-802.961	-802.076
-822.635	-824.200
-488.280	-489.409
-596.497	-598.458
-687.686	-688.438
-664.380	-664.180
-641.577	-640.622
-712.281	-711.734
-782.489	-782.000
-431.872	-431.062
	$\begin{array}{r} \Delta_{\rm f} {\rm H}^{\circ}({\rm RCl}_2,{\rm cr},{\rm 0})\\ -501.900\\ -554.807\\ -669.969\\ -693.128\\ -754.793\\ -802.961\\ -822.635\\ -488.280\\ -596.497\\ -687.686\\ -664.380\\ -641.577\\ -712.281\\ -782.489\\ -431.872\\ \end{array}$

TABLE 55 Reference data for the **e**nthalpies of formation of crystalline lanthanide dichlorides $(kJ/mol)^a$

^a Data have an accuracy of 0.001 kJ/mol, as accepted in IVTANTERMO (2004).

9. THERMODYNAMIC PROPERTIES OF LANTHANIDE DICHLORIDES

Studies of reactions that occur in the gas phase during the vaporization of $R + EuCl_2$ and $R + BaCl_2$ mixtures (R = Ce-Nd, Sm-Lu) (Chervonnyi, 1977a,b) and, more recently, of the La + BaCl₂ mixture (Chervonnyi and Chervonnaya, 2004b) showed that the formation of gaseous dichlorides at high temperatures is characteristic of all lanthanides. This substantiated previous measurements of the IEs and the appearance energies of the corresponding ions in electron-impact-ionized vapors of R + EuCl₂ and $R + RCl_2$ mixtures (Evdokimov et al., 1984; Sapegin, 1984; Sapegin et al., 1984). At the same time, thermodynamic parameters were determined from saturated vapor pressure measurements for four lanthanide dichlorides only. The vaporization of neodymium dichloride was studied by mass spectrometry by Kudin et al. (1993b). Similar experiments were performed several times for samarium, europium, and ytterbium dichlorides; the results obtained are reviewed by Chervonnyi and Chervonnaya (2004a,e,f, 2005b). These authors noted that data on the thermodynamic functions of condensed RCl₂ have not been included in most authoritative handbooks (Chase, 1998; IVTANTERMO, 2004). Only one handbook (Barin, 1995) contains the results of calculations performed for YbCl₂ over the temperature range 298.15–1000 K.

Several approximate calculations of thermodynamic functions can be found for EuCl₂ (Hariharan and Eick, 1972; Pogrebnoi and Kudin, 2003b) and for YbCl₂ (Hariharan et al., 1972). It was, however, shown (Chervonnyi and Chervonnaya, 2004a,e,f, 2005b) that these functions are not able to reconciliate the enthalpies of atomization of RCl₂ calculated from saturated vapor pressure measurements and those determined from the appearance energies AE(R⁺/RCl₂) or the equilibrium constants of the corresponding gas-phase reactions. Satisfactory accuracy could not be attained, although we preliminarily described the thermodynamic functions of gaseous lanthanide dichlorides (Chervonnyi and Chervonnaya, 2003, 2004c) and critically selected the standard enthalpies of formation $\Delta_{\rm f}H^{\circ}({\rm RCl}_2, {\rm cr}, 298)$ to exclude errors related to the use of other auxiliary values (Chervonnyi and Chervonnaya, 2005c).

These difficulties and the absence of systematic data on the thermodynamic functions of all compounds of the RCl₂ series prompted us to make an attempt to fill this gap (Chervonnyi and Chervonnaya, 2008a). Simultaneously, our purpose was to verify the effectiveness of the scheme suggested in Chervonnyi and Chervonnaya (2007a,b) for the description of the temperature dependence of heat capacities over the temperature range 0 K– T_m , this time for compounds in which lanthanides were in a different valence state. The main results of this investigation are described in this section.

9.1 Estimates of standard entropy values in condensed state

The unreliability and inconsistency of the available initial data for thermodynamic function calculations are already revealed from a comparison of the entropies at standard temperature $S^{\circ}(298)$, which substantially influence the reduced Gibbs energies used in calculations of the enthalpies of sublimation by the third law of thermodynamics.

The *S*°(298) value for EuCl₂ was estimated by Hariharan and Eick (1972) at 144.35 J/(mol·K). This estimate was based on a comparison with the thermochemical properties of BaCl₂, Ba, and Eu. Such a high value was obtained because of the inclusion of the additional magnetic contribution of Eu²⁺ (~17.3 J/(mol·K)). Comparative estimates of *S*°(298) for YbCl₂ were obtained by Hariharan et al. (1972) on the basis of the thermochemical properties of CaCl₂, Ca, and Yb; the resulting selected value was 122.59 J/(mol·K).

Several authors (Gavrichev et al., 1987a,b; Tolmach et al., 1986, 1987a,b) measured the low-temperature heat capacity of several lanthanide dichlorides (NdCl₂, SmCl₂, EuCl₂, DyCl₂, TmCl₂, and YbCl₂) over the temperature range from ~5 to ~342 K and calculated the *S*°(298) values for these dichlorides. Tolmach et al. (1988) corrected their results for incompletely determined excess contributions caused by cooperative magnetic ordering in EuCl₂ and excited electronic states of the other RCl₂. These corrections did not modify the data on SmCl₂ and YbCl₂. On the other hand, the *S*°(298) value for europium dichloride changed from 121.2 \pm 0.3 to 138.3 \pm 0.8 J/(mol·K), representing a 14% increase.

Later, Konings (2002) corrected the $S^{\circ}(298)$ values from Gavrichev et al. (1987a,b) and Tolmach et al. (1986, 1987a,b, 1988) and proposed estimates for the other RCl₂ compounds. These calculations were performed by representing the standard entropy as the sum of the lattice $S_{lat}^{\circ}(298)$ and excess $S_{exs}^{\circ}(298)$ contributions; the latter took into account excited electronic states. The $S_{lat}^{\circ}(298)$ values were found from linear dependences on the atomic number of lanthanides; two reference values were those for EuCl₂ and YbCl₂ from Tolmach et al. (1986, 1987b), which were assumed to be purely lattice contributions. The third reference value was the entropy of BaCl₂ from Goodman and Westrum (1966). The $S_{exs}^{\circ}(298)$ contributions were calculated using the electronic excitation energies of the 4f shells of free R²⁺ ions. The $S^{\circ}(298)$ values found were higher than those reported by Tolmach et al. (1988) for several compounds such as NdCl₂, TmCl₂, and EuCl₂, although for the latter, the discrepancy was very small, with $S^{\circ}(298) = 138.5$ J/(mol·K).

The approach to estimating entropies used by Konings (2002) encounters objections. First, according to what was found for lanthanide trifluorides and trichlorides (Chervonnyi and Chervonnaya, 2007a,b), the lattice contribution to entropy S_{lat}° (298) is a linear function of the molar volume

(see, for instance, Westrum et al., 1989), which, in turn, is a linear function of the atomic number of lanthanides, but only within a series of compounds with the same crystal lattice type. The reference compounds were therefore selected incorrectly, they did not satisfy this requirement. Second, calculations of the excess contribution $S_{exs}^{\circ}(298)$ from the spectral data on free R^{2+} ions (without taking into account the splitting of the ground state by ligand field) results in noticeable errors. Nevertheless, the closeness of the results obtained by Tolmach et al. (1988) and Konings (2002) allows a parallel to be drawn between them.

The lattice contributions calculated by Konings (2002) can be thought to be close to those that can be determined from the experimental data (Gavrichev et al., 1987a,b; Tolmach et al., 1986, 1987a,b). Conclusions concerning the reliability of the experimental data can therefore be based on the difference between the lattice terms obtained for lanthanide tri- and dichlorides. This difference is determined by the contribution of the Cl⁻ anion to the lattice entropy component. This value should vary insignificantly, especially in series of related compounds. A comparison of pairs of compounds with isoelectronic cations seems to be a more correct approach. We therefore subtracted the $S_{lat}^{\circ}(RCl_2, 298)$ values found by Konings (2002) from the calculated $S_{lat}^{\circ}(RCl_3, 298)$ values that we reported (Chervonnyi and Chervonnaya, 2007b). The differences obtained were 22.96 J/(mol·K) for the pair LuCl₃–YbCl₂, 13.04 J/(mol·K) for GdCl₃–EuCl₂, and 12.92 J/(mol·K) for EuCl₃–SmCl₂.

The value for the first pair is close to the contribution of the Cl⁻ anion (24.96 J/(mol·K)) obtained by Sommers and Westrum (1977) in analyzing methods for estimating entropies. In our analysis of the thermodynamic properties of YbCl₂ (Chervonnyi and Chervonnaya, 2004f), we also did not encounter difficulties with the use of the standard entropy from Tolmach et al. (1987b). As far as the other pairs are concerned, the underestimated values by ~10 J/(mol·K) are rather indicative of serious errors in low-temperature heat capacity values, at least, for SmCl₂ (Gavrichev et al., 1987b) and EuCl₂ (Tolmach et al., 1986). This is the reason why we reported analyses of the thermochemical parameters (enthalpies of sublimation and atomization) of samarium and europium dichlorides were using the thermodynamic functions calculated with $S^{\circ}(298) = 122.59$ and 127.85 J/(mol·K) for SmCl₂ and EuCl₂, respectively (Chervonnyi and Chervonnaya, 2004a,e, 2005b).

9.2 Heat capacity calculations

The compounds under consideration form crystal lattices of three types (Meyer, 1988). According to X-ray structure data, NdCl₂, SmCl₂, and EuCl₂ have lattices of the PbCl₂ structure type with the CN of the cation equal to 9. DyCl₂ forms a SrBr₂-type crystal lattice with the metal in

having CN = 8 (Meyer, 1988). According to Astakhova and Goryushkin (1992), this structure type is also characteristic of GdCl₂ and TbCl₂. Crystal structures of the third type (SrI₂, CN = 7) were experimentally observed for HoCl₂, TmCl₂, and YbCl₂. In addition, according to the estimates made by Astakhova and Goryushkin (1992), structures of the first type can be formed by cerium, praseodymium, and promethium dichlorides, and a structure of the third type by erbium dichloride. In addition to structural data, experimental or estimated molar volumes V_{RCl_2} (see Table 56) were reported by Astakhova and Goryushkin (1992). As with RF₃ and RCl₃, the V_{RCl_2} parameter changed monotonically with the atomic number of the lanthanide over a series of isostructural compounds. It changed jumpwise in passing to another structure type and then again increased monotonically.

Calculations of the contribution from the lattice heat capacity $C_{lat}(T)$ were performed by Chervonnyi and Chervonnaya (2007a,b) in the quasiharmonic approximation showed that the characteristic parameters of this approximation linearly depend on the molar volume and change jumpwise in passing from one structure type to another. We made an attempt at determining similar trends in the experimental data (Gavrichev et al., 1987a,b; Tolmach et al., 1986, 1987a,b), especially that the series of lanthanide dichlorides studied in these works represented a fairly representative selection. It contained three compounds with the first (NdCl₂, SmCl₂, and EuCl₂) and third (DyCl₂, TmCl₂, and YbCl₂) crystal structure types. In addition, no Schottky anomaly was observed for diamagnetic ytterbium dichloride.

The data obtained by Gavrichev et al. (1987a,b) and Tolmach et al. (1986, 1987a,b) were processed with the subtraction (if necessary!) of the excess contributions to heat capacity $C_{exs}(T)$ from experimental heat

R	CN	V _{RCl₂}	R	CN	V _{RCl₂}
La	9	49.84 ^a	Tb	8	46.80 ^a
Ce	9	48.91	Dy	7	48.38
Pr	9	47.96	Ho	7	47.70
Nd	9	47.06	Er	7	47.02
Pm	9	46.08	Tm	7	46.23
Sm	9	45.16	Yb	7	45.78
Eu	9	44.24	Lu	7	45.02 ^a
Gd	8	45.56 ^a	_	_	-

TABLE 56 Coordination numbers of R^{2+} cations and molar volumes (V_{LnCl_2} , cm³/mol) of lanthanide dichlorides; data from Astakhova and Goryushkin (1992)

^a Our estimate.

capacity values $C_{p, \exp}^{\circ}(T)$. Excess contributions arise from the presence of electronically excited states in the compounds under consideration. The $C_{exs}^{\circ}(T)$ values were calculated according to the classical theory (see Section 4 for details). The initial data for these calculations were the energies of the excited electronic states of the R²⁺ ions in the crystal field of Cl⁻ ligands and free R²⁺ ions (see Table 7).

The temperature dependence of the $(C_{p, exp}(T) - C_{exs}(T))$ difference obtained, which was the lattice heat capacity component, was approximated by Eq. (6).

The number of atoms in the RCl₂ molecule being known, the parameters to be determined were θ_D , θ_{E1} , θ_{E2} , and α . The accuracy of approximate calculations was controlled using the χ^2 statistical test (see Section 5).

Next, we studied trends in characteristic parameter variations depending on the molar volume. This allowed us not only to estimate the reliability of the data available in (Gavrichev et al., 1987a,b; Tolmach et al., 1986, 1987a,b) but also to select suitable θ_D , θ_{E1} , θ_{E2} , and values (including values for unstudied compounds) according to the suggested criteria. These values were then used to calculate the temperature dependences of heat capacities by Eq. (9).

9.2.1 Experimental data processing

We approximated 113 heat capacities of YbCl₂ measured by Tolmach et al. (1987b) over the temperature range 7.55–315.04 K to obtain characteristic values (see Table 57) with a fairly small χ^2 , which was evidence of a close agreement between calculated and experimental data. Indeed, calculations by Eq. (6) with the θ_D , θ_{E1} , θ_{E2} , and α values found gave ($C_{p, cal}^{\circ}(298) - C_{p, exp}^{\circ}(298)$) differences as small as 0.02 J/(mol·K). The difference between the experimental and calculated entropy values under standard conditions was the same (see Table 58).

Calculations of the characteristic parameters for DyCl₂ from the experimental data of Tolmach et al. (1987a) showed that, after subtracting the $C_{exs}^{\circ}(T)$ contribution, the difference curve (122 values over the temperature range 8.46–342.9 K) was less well approximated. The χ^2 value was an order of magnitude larger than for YbCl₂.

The same approximation procedure applied to 111 values obtained for TmCl₂ after the subtraction of $C_{exs}^{\circ}(T)$ from experimental measurements over the temperature range 6.52–339.42 K (Tolmach et al., 1987a) gave a χ^2 value lower than that obtained for DyCl₂.

The set of characteristic parameters obtained for DyCl₂, TmCl₂, and YbCl₂ could not be used to obtain the expected trends of their changes with respect to the molar volume. The spread of these data was too large. We therefore performed $C_{lat}^{\circ}(T)$ calculations for DyCl₂ according to (6). The θ_D , θ_{E1} , θ_{E2} , and α values were adjusted in such a way that, after the determination of $C_{lat}^{\circ}(T)$, the $(S_{lat}^{\circ}(RCl_3, 298) - S_{lat}^{\circ}(RCl_2, 298))$ difference

				α $ imes$ 10 ⁶	χ ² (J ² /	
R	Θ_{D} (K)	$\Theta_{ t E1}(ext{cm}^{-1})$	$\Theta_{E2}(cm^{-1})$	(mol∕J)	(mol·K)²)	References ^a
La	130.84905	146.49584	228.76513	2.84498	_	-
Ce	131.46863	147.76776	232.21444	2.85691	_	_
Pr	132.10153	149.06704	235.73794	2.86909	_	_
Nd	132.59082	150.19348	238.97151	2.88063	_	_
Pm	133.35400	151.63824	242.71074	2.89320	_	_
Sm	120.69158	127.70855	211.18495	1.74977	0.06937	b
	134.30451	153.21700	246.44347	2.90500	_	_
Eu	117.45119	134.12180	206.91498	2.21480	0.02024	С
	134.35218	153.93892	249.31936	2.91680	_	_
Gd	129.29092	145.11750	237.88130	2.85344	_	-
Tb	124.53655	136.83059	227.13636	2.79392	_	_
Dy	118.47873	140.32867	218.01037	3.30300	0.13785	d
5	118.47873	126.27133	213.44509	2.71809	_	_
Но	118.91332	127.17463	215.94031	2.72681	_	_
Er	119.34769	128.07779	218.43554	2.73553	_	-
Tm	139.15742	104.22449	230.74395	2.45662	0.05543	d
	119.85233	129.12704	221.33441	2.74566	_	_
Yb	120.13957	129.72458	222.98566	2.75143	0.01450	е
	120.13957	129.72458	222.98566	2.75143	_	-
Lu	120.62525	130.73413	225.77444	2.76118	-	_

TABLE 57Characteristic parameters for calculations of the lattice contribution to the
heat capacity of lanthanide dichlorides

^{*a*} References are given to the works in which Θ_D , Θ_{E1} , Θ_{E2} , α , and χ^2 values were obtained by experimental data processing; for the other compounds, values selected in this work are given. Einstein characteristic temperature is more conveniently represented by Einstein's oscillator frequency; frequency can be converted to temperature by using a factor of 1.43879 K cm.

^b Gavrichev et al. (1987b).

^c Tolmach et al. (1986).

^d Tolmach et al. (1987a).

^e Tolmach et al. (1987b).

for the HoCl₃–DyCl₂ pair coincided with that for the LuCl₃–YbCl₂ pair (~22.77 J/(mol·K)). We also imposed that changes in the characteristic parameters depending on the molar volume be the same as those determined in our work (Chervonnyi and Chervonnaya, 2007a,b). In this and subsequent calculations, the lattice contributions to the $S_{lat}^{\circ}(298)$ standard entropy values were obtained by the integration of the $C_{lat}^{\circ}(T)/T$ ratio over the temperature range 0–298.15 K. As follows from Table 57, which lists the characteristic parameters selected in this way, the Debye temperature only coincided with that found by processing experimental data (Tolmach et al., 1987a).

The characteristic parameters calculated in this way for DyCl₂ and YbCl₂ were then used as reference values for determining θ_{D} , θ_{E1} , θ_{E2} , and

	S [°] _{exs} (298)	C° _p (298)	S _{lat} (298)	S°(298)	C _P (298)	<i>S</i> °(298)	References	S [°] _{exs} (298)	S _{lat} (298)	S°(298)
R	Our calculations			Experimental			Data from Konings (2002)			
La	11.574	75.82	114.36	125.94	_	_	_	14.9	123.2	138.09
Ce	18.129	76.26	113.70	131.80	-	-	_	18.27	122.93	141.2
Pr	18.805	77.03	113.02	131.78	-	-	_	19.14	122.67	141.82
Nd	18.392	77.20	112.44	130.82	77.77 ± 0.10	135.3 ± 0.2	а	18.27	122.41	140.68
	_	_	_		77.77 ± 0.30	140.1 ± 0.5	b	-	-	-
Pm	15.922	78.64	111.72	127.69	-	-	_	17.29	122.15	139.44
Sm	11.647	84.64	110.94	122.59	84.60 ± 0.10	132.2 ± 0.1	С	9.32	121.89	131.21
	_	_	_		84.41 ± 0.30	132.2 ± 0.4	b	_	_	-
Eu	17.289	75.00	110.56	127.85	75.22 ± 0.10	121.2 ± 0.3	d	17.29	121.62	138.91
	_	_	_		75.23 ± 0.40	138.3 ± 0.8	b	_	_	-
Gd	20.587	82.10	113.99	134.58	_	_	_	21.32	121.36	142.69
Tb	22.890	75.92	117.38	140.28	_	_	_	23.05	121.1	144.15
Dy	23.222	76.60	121.99	145.21	77.30 ± 0.10	134.0 ± 0.2	е	23.56	120.84	144.39
-	_	_	_		77.30 ± 0.30	144.2 ± 0.6	b	_	_	-
Но	22.736	76.51	121.45	144.20	_	_	_	23.05	120.58	143.63
Er	20.989	76.53	120.93	141.93	_	_	_	21.32	120.31	141.64
Tm	16.738	76.77	120.32	137.07	76.98 ± 0.10	131.6 ± 0.2	е	17.29	120.05	137.34
	_	_	_		76.68 ± 0.20	135.1 ± 0.3	b	_	_	-
Yb	0	75.76	119.98	119.98	75.74 ± 0.10	120.0 ± 0.2	f	0	119.79	119.79
	_	_	_		75.73 ± 0.40	120.0 ± 0.6	b	_	_	-
Lu	5.763	75.70	119.40	125.17	_	_	-	-	_	-

TABLE 58 Standard heat capacities, entropies, and excess contributions to the entropies of lanthanide dichlorides $(J/(mol \cdot K))$

^{*a*} Gavrichev et al. (1987a). ^{*b*} Tolmach et al. (1988). ^{*c*} Gavrichev et al. (1987b). ^{*d*} Tolmach et al. (1987a). ^{*f*} Tolmach et al. (1987a). ^{*f*} Tolmach et al. (1987b). Note: For NdCl₂, the $S^{\mathbf{0}}(298) - S^{\mathbf{0}}(8)$ value is reported in Gavrichev et al. (1987a).

 α for other compounds with the same crystal structure type. Their values found from the linear dependence on molar volume are listed in Table 57. Calculations of the $C_{lat}^{\circ}(T)$ (Eq. (6)) and $C_{p}^{\circ}(T)$ (Eq. (9)) temperature dependences with these parameters gave $C_{p}^{\circ}(298)$, $S_{lat}^{\circ}(298)$, and $S^{\circ}(298)$ standard values. These data are listed in Table 58, which also contains similar results obtained by Tolmach et al. (Gavrichev et al., 1987a,b; Tolmach et al., 1986, 1987a,b) and Konings (2002).

It follows from a comparison of these values that the mutual deviations for DyCl₂ and TmCl₂ are fairly small. For heat capacities, these deviations are in the range ~0.2–0.7 J/(mol·K), and for entropy, ~1–2 J/(mol·K). Note that the $(S_{lat}^{\circ}(\text{RCl}_3, 298) - S_{lat}^{\circ}(\text{RCl}_2, 298))$ difference obtained in our calculations for the YbCl₃–TmCl₂ pair is 22.58 J/(mol·K).

The most reliable characteristic parameters for compounds of the other crystal structure types can be obtained by processing the experimental data on samarium and europium dichlorides. Indeed, the cooperative magnetic transition characteristic of the Eu²⁺ ion in europium dichloride should be observed at temperatures lower than the minimum temperature limit at which heat capacity measurements have been performed by Tolmach et al. (1986). It follows that these data can be treated as the lattice contribution to the heat capacity of EuCl₂.

As concerns SmCl₂, because of the absence of splitting of the ground 4f level in Sm²⁺ and a fairly high energy of the first electronically excited state, the temperature dependence of the excess contribution to heat capacity is a smooth curve. Over the temperature range from ~50 to ~200 K, this contribution smoothly increases from zero and reaches a plateau at $T \sim 250$ K when its value is about 8 J/(mol·K). The subtraction of such a contribution from the experimental heat capacity curve for the determination of the characteristic parameters should not distort their values substantially.

We were indeed able to process the experimental data on EuCl₂ very accurately. Heat capacity values (107 measurements performed by Tolmach et al. (1986) over the temperature range from 6.58 to 310.86 K) were approximated with a very low χ^2 -test value. The lattice contribution to the heat capacity of SmCl₂ (107 measurements over the temperature range from 5.98 to 302.16 K; Gavrichev et al., 1987b) was also approximated satisfactorily. Conversely, after the excess contribution was subtracted from the experimental data on NdCl₂ (Gavrichev et al., 1987a), we found that the first 14 values over the temperature range from 7.6 to 24.43 K gave unrealistic lattice contribution values. On the other hand, calculations without these values strongly decreased the accuracy of the determination of the characteristic parameters, in the first place, the θ_D value.

Considering that the molar volumes of SmCl₂, EuCl₂, and YbCl₂ are close to each other, a comparison of the characteristic parameters of these three compounds should reveal an obvious discontinuous increase for

samarium and europium dichlorides compared with ytterbium dichloride. In reality, the expected jump is only observed for θ_D of SmCl₂ and θ_{E1} of EuCl₂. This generates the impression that CN decreases rather than increases in these compounds.

A similar phenomenon was previously observed for lanthanide chlorides, however, under very unusual conditions (Stumpp, 1977; Suzuki et al., 1991). A study of the crystal structure and magnetic properties of SmCl₃, EuCl₃, DyCl₃, HoCl₃, ErCl₃, TmCl₃, YbCl₃, and LuCl₃ intercalated into graphite showed that samarium and europium trichlorides, which have UCl₃-type (CN = 9) crystal structures under usual conditions, formed YCl₃-type (CN = 6) crystal structures in graphite; such structures are characteristic of lanthanide trichlorides from Dy to Lu under normal conditions. As to the other lanthanide trichlorides studied, their structure remained unchanged.

The behavior of the characteristic parameters in the series of RCl₂ compounds can be explained if we consider the synthetic procedure used by Gavrichev et al. (1987a,b) and Tolmach et al. (1986, 1987a,b). The EuCl₂ and YbCl₂ samples were obtained by reducing anhydrous lanthanide trichlorides with hydrogen. The other compounds were prepared by sintering (melting together) trichlorides with the corresponding lanthanides. Reaction completion was controlled by measuring X-ray powder patterns, and the stoichiometry of the products, by chemical analysis. It, however, follows from the mass spectra of the gas phase and saturated vapor pressure measurements (Chervonnyi et al., 1975; Il'in et al., 1973) over SmCl₂, EuCl₂, and YbCl₂ that the samples obtained by reduction always contain small amounts of the corresponding trichlorides. Supposedly, the synthesis of NdCl₂, SmCl₂, DyCl₂, and TmCl₂ by sintering suffers from the same shortcoming. It may well be that this factor determines the appearance of such unusual dependences of the characteristic parameters for crystal structures of two different types.

In our view, applying the approximation to the experimental data on NdCl₂ (Gavrichev et al., 1987a), SmCl₂ (Gavrichev et al., 1987b), and EuCl₂ (Tolmach et al., 1987a) gave unrealistic characteristic parameter values. We therefore decided to determine them by fitting.

Taking into account the results obtained earlier (Chervonnyi and Chervonnaya, 2007a,b) for similar compounds, we selected the characteristic parameters that satisfied several criteria. First, these values had to depend linearly on the molar volume, and the parameters had to increase in going to structures with CN = 9. Second, the $(S_{lat}^{\circ}(RCl_3, 298) - S_{lat}^{\circ}(RCl_2, 298))$ difference for pairs of compounds with isoelectronic cations (PmCl₃–NdCl₂, EuCl₃–SmCl₂, and GdCl₃–EuCl₂) had to be close to the value recommended by Sommers and Westrum (1977). Third, the enthalpies of sublimation calculated using the thermodynamic functions obtained from the temperature dependences of heat capacities had to be in agreement with the results of independent measurements.

The successive approximation method was used to determine the characteristic parameters of dichlorides with PbCl₂-type structures (see Table 57). Calculations of standard heat capacities with the use of these parameters gave values that did not differ substantially from measurement results (Gavrichev et al., 1987a,b; Tolmach et al., 1986, 1987a,b). According to Table 58, the ($C_{p, cal}^{\circ}(298) - C_{p, exp}^{\circ}(298)$) differences were -0.57, 0.04, and -0.22 J/(mol·K) for NdCl₂, SmCl₂, and EuCl₂, respectively. More substantial deviations were observed for the *S*°(298) values, especially after they were corrected in Tolmach et al. (1988). Our calculations gave values that were lower by ~ 10 J/(mol·K) compared to those obtained by Tolmach et al. (1988).

The characteristic parameters selected for this structural group of compounds gave ($S_{lat}^{\circ}(RCl_3, 298) - S_{lat}^{\circ}(RCl_2, 298)$) entropy differences between compounds with isoelectronic cations of 23.17, 23.87, and 24.19 J/(mol·K) for the PmCl₃–NdCl₂, EuCl₃–SmCl₂, and GdCl₃–EuCl₂ pairs, respectively. These values are closer to the contribution of the Cl⁻ anion proposed by Sommers and Westrum (1977) than those obtained above for the HoCl₃–DyCl₂, YbCl₃–TmCl₂, and LuCl₃–YbCl₂ pairs.

It is interesting to compare the $(C_{p, exp}^{\circ}(T) - C_{lat}^{\circ}(T))$ differences calculated using the characteristic parameters recommended in this work at every temperature of measurements and the $C_{exs}^{\circ}(T)$ values calculated by the classical scheme for the excited electronic states of the R²⁺ and R³⁺ ions. The corresponding curves are shown in Figures 30 and 31 for NdCl₂ and TmCl₂, respectively. We believe that the appearance of an unforeseen excess contribution to the heat capacity of these compounds is likely determined by the presence of the corresponding trivalent cations in the samples studied experimentally (Gavrichev et al., 1987a; Tolmach et al., 1987a). Similar calculations for DyCl₂ give $(C_{p, exp}^{\circ}(T) - C_{lat}^{\circ}(T))$ values that depend on temperature somewhat differently from the corresponding values obtained for NdCl₂ and TmCl₂. This dependence presents a maximum at 250–300 K, which we cannot explain for the time being.

The behavior of $(C_{p, exp}^{\circ}(T) - C_{lat}^{\circ}(T))$ for TmCl₂ casts doubts on the reliability of the experimental data reported for DyCl₂ and YbCl₂, which were processed to obtain the reference characteristic parameter values for dichlorides of this structural group. Indeed, the following circumstance indirectly leads us toward the same conclusion.

A comparison of the linear dependences obtained for the characteristic parameters of compounds with PbCl₂- and SrI₂-type crystal structures shows that changes in θ_D , θ_{E1} , θ_{E2} , and α accompanying the passage from one structure type to the other are too large compared with those found earlier for RF₃ and RCl₃. Higher characteristic parameter values for



FIGURE 30 Excess contribution to the heat capacity of $NdCl_2$: (1) calculations for the Nd^{2+} ion and (2) calculations for the Nd^{3+} ion; open circles are found from treatment of the experimental data from Gavrichev et al. (1987a). Reproduced from Chervonnyi and Chervonnaya (2008a) with permission from Pleiades Publishing, Ltd.

Dy–Yb dichlorides would make the $(S_{lat}^{\circ}(RCl_3, 298) - S_{lat}^{\circ}(RCl_2, 298))$ differences for the HoCl₃–DyCl₂, YbCl₃–TmCl₂, and LuCl₃–YbCl₂ pairs larger, that is, closer to the estimate obtained by Sommers and Westrum (1977). Seemingly, we had to additionally refine the θ_D , θ_{E1} , θ_{E2} , and α values for RCl₂ with SrI₂-type crystal structures. We, however, eschewed to do this, mainly because the thermodynamic functions of YbCl₂ calculated from the data obtained by Tolmach et al. (1987b) gave satisfactory agreement between the enthalpies of atomization calculated from saturated vapor pressure measurements and obtained by independent methods (Chervonnyi and Chervonnaya, 2004f).

The characteristic parameters in the RCl₂ series were described assuming that GdCl₂ and TbCl₂ had transition structures with CN = 8 (SrBr₂ type). The molar volumes for them (see Table 56) were estimated on the assumption of a linear dependence of molar volume changes on the atomic number of lanthanides. Next, these *V* values were used to estimate the characteristic parameters of gadolinium and terbium dichlorides; their values are given in Table 57. The obtained values for θ_D , and α are shown in Figures 32 and 33 as functions of the molar volumes for three series of RCl₂.



FIGURE 31 Excess contribution to the heat capacity of $TmCl_2$: (1) calculations for the Tm^{2+} ion and (2) calculations for the Tm^{3+} ion; open circles are found from treatment of the experimental data from Tolmach et al. (1987a). Reproduced from Chervonnyi and Chervonnaya (2008a) with permission from Pleiades Publishing, Ltd.



FIGURE 32 Dependence of the $\theta_{\rm D}$ values on molar volume in the series of RCl₂ compounds.



FIGURE 33 Dependence of the α values on molar volume in the series of RCl_2 compounds.

9.2.2 Determination of the $C_{d, cor}^{\circ}(T)$ contribution

The systematic bias leading to a lowering of the high-temperature $C_{p,cal}^{\circ}(T)$ values at $T > \sim 0.5T_{\rm m}$ caused by the use of the quasi-harmonic approximation in calculating the lattice heat capacity contribution was taken into account by Chervonnyi and Chervonnaya (2007a,b) by comparing the $C_{p,cal}^{\circ}(T)$ and $C_{p,exp}^{\circ}(T)$ values (the latter being obtained from high-temperature measurements of either heat capacity or enthalpy increments).

The $C_{d, cor}^{\circ}(T)$ contribution for lanthanide dichlorides can be estimated by comparing $C_{p, cal}^{\circ}(T)$ and $C_{p, exp}^{\circ}(T)$ only in the case of EuCl₂, for which the corresponding experimental data are available (Da Silva et al., 2001). A differential scanning calorimeter was used by these authors to determine not only the $\beta \rightarrow \alpha$ and $\alpha \rightarrow$ liq phase transition parameters but also heat capacities in the regions of the existence of the β and α polymorphs (T = 306-1085 K). The heat capacity of the β polymorph was approximated by the linear equation $C_{p}^{\circ}(\beta-\text{EuCl}_{2}, T)$, $J/(\text{mol}\cdot\text{K}) = 68.27 + 0.0255$ T (306 < T < 900 K). It, however, follows from the plots presented by Da Silva et al. (2001) that heat capacity measurements were performed over a temperature interval wider than that within which heat capacities were processed analytically. The $C_{p, exp}^{\circ}(T)$ values did not obey the linear law for T < 400 K and T > 900 K (see Figure 34).



FIGURE 34 High-temperature heat capacity data for the α - (inset) and β -EuCl₂ polymorphs. Open circles are the experimental data from Da Silva et al. (2001); the solid line represents accepted values from the calculation of thermodynamic functions and the dashed line corresponds to values calculated by Eq. (9). Reproduced from Chervonnyi and Chervonnaya (2008a) with permission from Pleiades Publishing, Ltd.

We digitized the plots from Da Silva et al. (2001) to explore all the special features of the behavior of $C_{p, exp}^{\circ}(T)$ over the complete temperature range of measurements. The difference between $C_{p, exp}^{\circ}(T)$ and $C_{p, cal}^{\circ}(T)$ at T > 520 K was then normalized by the molar volume of EuCl₂ and approximated using a polynomial of the form $(a + bT + cT^2)$. The dependence was then multiplied by the molar volumes of RCl₂ to obtain the $C_{d, cor}^{\circ}(T)$ corrections to the heat capacities of lanthanide dichlorides,

$$C_{\rm d,cor}^{\circ}(T) = V_{\rm RCl_2} \left(-7.016 \times 10^{-2} + 1.40045 \times 10^{-4} T - 8.2159 \times 10^{-9} T^2 \right). \tag{29}$$

Eventually, the temperature dependences of the heat capacities of RCl₂ over the complete temperature range were determined by Eq. (11) by summing three contributions calculated as: $C_{lat}^{\circ}(T)$, using the (θ_D , θ_{E1} , θ_{E2} , and α characteristic parameters; $C_{exs}^{\circ}(T)$, using the electronic excitation energies from Table 7; and $C_{d, cor}^{\circ}(T)$, according to Eq. (29) at all temperatures at which $C_{d, cor}^{\circ}(T) > 0$.

9.2.3 Temperatures and enthalpies of phase transitions

Available experimental data (Caro and Corbett, 1969; Corbett and McCollum, 1966; Brixner and Bierlein, 1974; Da Silva et al., 2001; Druding and Corbett, 1961; Dworkin and Bredig, 1971; Goryushkin, 1996; Goryushkin and Poshevneva, 1991; Goryushkin et al., 1990d, 1991; Jantsch et al., 1927; Kapfenberger, 1938; Kulagin and Laptev, 1976; Laptev, 1996; Laptev et al., 1975, 1976a,b, 1979; Polyachenok and Novikov, 1963a, b,c; Spedding and Daane, 1960) were analyzed on the assumption that the main criterion for estimating phase transition parameters was the correlation proposed by Dworkin and Bredig (1971) between the crystal structure type and the entropy of the phase transition. If a compound undergoes two phase transitions ($\beta \rightarrow \alpha$ and $\alpha \rightarrow$ liq), the sum of the entropies of these transitions ($\Delta_{tr}S^{\circ} + \Delta_mS^{\circ}$) was taken into account; here, $\Delta_{tr}S^{\circ}$ is the entropy of the phase transition from the β to α polymorph and Δ_mS° is the entropy of α polymorph transition into the liquid state. It was found that, for related lanthanide compounds with the same structure, this parameter was constant.

Indeed, if this parameter is determined from the data selected by Chervonnyi and Chervonnaya (2007b) to calculate the thermodynamic functions of lanthanide trichlorides, the ($\Delta_{tr}S^{\circ} + \Delta_mS^{\circ}$) values fall inside the interval 48.8 ± 1.6 J/(mol·K) for hexagonal RCl₃ (R = La–Gd) with CN = 9. As far as monoclinic RCl₃ (R = Dy–Lu) with CN = 6 are concerned, ($\Delta_{tr}S^{\circ} + \Delta_mS^{\circ}$) is found to be 31.7 ± 2.5 J/(mol·K). Similar dependences on the structure type of crystal lattices are observed for RF₃. According to Chervonnyi and Chervonnaya (2007a), the sum of the entropies of phase transitions is within the interval 33.1 ± 1.0 J/(mol·K) for RF₃ (R = La–Pm) and 40.6 ± 2.2 J/(mol·K) for RF₃ (R = Sm–Lu).

A comparison of the entropies of phase transitions of lanthanide trichlorides and trifluorides shows that, among related compounds, this parameter is higher for structures with larger cation CN values. Provided that lanthanide dichlorides are characterized by the same trend, the conclusion can be drawn that the entropies of melting or the sums of the entropies of phase transitions should be approximately equal for RCl₂ (R = Ce–Eu) and RCl₂ (R = Dy–Yb). As the cation CN is higher in the first group (PbCl₂-type structures with CN = 9) than in the second group (SrI₂-type structures with CN = 7), the entropies of the phase transition should be higher for the first group.

The conclusions that can be drawn from the experimental data cited above are as follows.

First, results for six lanthanide dichlorides only (R = Nd, Sm, Eu, Dy, Tm, and Yb) were obtained. Goryushkin et al. (1989c, 1992a) made repeated attempts to synthesize HoCl₂ and study its physicochemical properties. The structure of this compound was found to be similar to that of dysprosium, thulium, and ytterbium dichlorides, but the authors were unable to isolate it in pure form. Studies of its phase transition revealed the occurrence of incongruent melting with the appearance of holmium metal in the melt at 874 ± 4 K. Holmium finally dissolved in the salt melt at 1228 ± 5 K. More recently (Goryushkin, 1996), the enthalpy of incongruent melting of HoCl₂ was estimated at 13.7 kJ/mol.

Two dichlorides, NdCl₂ and DyCl₂, melt incongruently (Goryushkin, 1996), and SmCl₂ and EuCl₂ experience the $\beta \rightarrow \alpha$ transition at high temperatures (Astakhova and Goryushkin, 1992). Their high-temperature polymorphs have fluorite-type structures (CN = 8) and are less compact than the low-temperature β -polymorphs (the molar volumes of α -SmCl₂ and α -EuCl₂ are 55.04 and 55.05 cm³/mol, respectively). The $\beta \rightarrow \alpha$ transition is accompanied by an increase in volume by ~24%.

Second, in several works (Caro and Corbett, 1969; Corbett and McCollum, 1966; Brixner and Bierlein, 1974; Druding and Corbett, 1961; Jantsch et al., 1927; Kapfenberger, 1938; Polyachenok and Novikov, 1963a, b,c; Spedding and Daane, 1960), only phase transition temperatures are reported. There are phase transitions interpreted as melting the temperatures of which are lower than or close to the $\beta \rightarrow \alpha$ transition temperature. This is, in particular, characteristic of the SmCl₂ melting point reported to be $T_m = 1013$ K (Jantsch et al., 1927); this value should be compared with the results obtained by Laptev et al. (1976a,b) and Goryushkin (1996). The same follows from a comparison of the data on EuCl₂, 1004 K (Spedding and Daane, 1960), 1011 K (Polyachenok and Novikov, 1963b), and 1030 K (Brixner and Bierlein, 1974) with phase transition temperature measurements performed by several authors (Da Silva et al., 2001; Goryushkin, 1996; Koyama et al., 1997).

Next, Goryushkin (1996) suggested that the melting points of dichlorides change in opposite direction to the melting points of lanthanide trichlorides. Note that this trend is not seen very clearly from the data reported by several authors (Caro and Corbett, 1969; Corbett and McCollum, 1966; Da Silva et al., 2001; Druding and Corbett, 1961; Goryushkin, 1996; Goryushkin and Poshevneva, 1991; Goryushkin et al., 1990d, 1991; Kapfenberger, 1938; Koyama et al., 1997; Kulagin and Laptev, 1976; Laptev et al., 1975, 1976a,b, 1979; Polyachenok and Novikov, 1963a,c). The melting points reported for NdCl₂ (1114 K, Druding and Corbett, 1961; 1108 K, Polyachenok and Novikov, 1963a; and 1098.4 \pm 4.5 K, Goryushkin et al., 1991) fit into this pattern in spite of the incongruent character of melting, whereas the data for DyCl₂ (994 K, Corbett and McCollum, 1966; 949 \pm 5 K, Goryushkin and Poshevneva, 1991) are obviously underestimated by ~100 K. The 970 K value reported by Spedding and Daane (1960) for TmCl₂ is also likely to be too low.

Last, the spread of the enthalpy values reported for NdCl₂ (Goryushkin et al., 1991), SmCl₂ (Goryushkin, 1996; Laptev, 1996; Laptev et al., 1976b, 1979), EuCl₂ (Da Silva et al., 2001; Goryushkin, 1996; Kulagin and Laptev, 1976; Laptev, 1996; Laptev et al., 1975; Koyama et al., 1997), DyCl₂ (Goryushkin and Poshevneva, 1991), TmCl₂ (Goryushkin et al., 1990d), and YbCl₂ (Goryushkin et al., 1990d; Laptev, 1996) is too large. The low values of this parameter for NdCl₂, 14.7 \pm 2.9 kJ/mol (Goryushkin et al., 1991) and DyCl₂, 13.4 \pm 2.6 kJ/mol (Goryushkin and Poshevneva, 1991) can

be explained by the formation of the metals in the initial sample melts (Goryushkin, 1996). At the same time, the low enthalpy of melting (14.2 kJ/mol) reported for SmCl₂ (Laptev, 1996; Laptev et al., 1979) and the high enthalpy of the $\beta \rightarrow \alpha$ transition (25.0 ± 5.0 kJ/mol) (Laptev et al., 1976b; Goryushkin, 1996) likely require substantial corrections. Likewise, the thermal constants for EuCl₂ (Da Silva et al., 2001; Goryushkin, 1996; Kulagin and Laptev, 1976; Laptev, 1996; Laptev et al., 1975; Koyama et al., 1997) and TmCl₂ (Caro and Corbett, 1969; Goryushkin et al., 1990d) should be selected with caution. The data reported for YbCl₂ (Laptev, 1996) agree well with those from other works (Goryushkin et al., 1990d; Polyachenok and Novikov, 1963b; Spedding and Daane, 1960) as concerns the melting point ($T_{\rm m} = 975$, 981, and 986.8 ± 2.9 K), but the enthalpies of melting found by Laptev (1996), 20.6 ± 0.7 kJ/mol, and by Goryushkin et al. (1990d), 31.5 ± 6.3 kJ/mol are fairly different.

Indeed, if the phase transition parameters reported by Goryushkin et al. (1990d) for YbCl₂ ($T_{\rm m} = 986.8 \pm 2.9$ K and $\Delta_{\rm m}H^{\circ} = 31.1 \pm 6.2$ kJ/ mol) are considered as being correct, the resulting $\Delta_{\rm m}S^{\circ} = 31.5$ J/(mol·K) value can be brought in agreement with the corresponding value for TmCl₂ under the following conditions. The melting point should be assumed to be 991 K (Caro and Corbett, 1969) rather than 987.0 \pm 3.4 K (Goryushkin et al., 1990d). It should in addition be assumed that the $\Delta_{\rm m}H^{\circ} = 35.0 \pm 7.0$ kJ/mol value from Goryushkin et al. (1990d) is exaggerated. For TmCl₂, a more realistic enthalpy of phase transition would be equal to $\Delta_{\rm m}H^{\circ}$ for YbCl₂. This selection is in agreement with the trends in variations of the temperature and enthalpy of phase transitions over the series of compounds under consideration. In addition, lowering $\Delta_{\rm m}H^{\circ}$ to 31.1 kJ/mol for TmCl₂ leaves this value within the uncertainty of the measurements reported by Goryushkin et al. (1990d).

Analysis of phase transition parameters ($\beta \rightarrow \alpha$ and $\alpha \rightarrow \text{liq}$) for SmCl₂ (Goryushkin, 1996; Laptev, 1996; Laptev et al., 1976b, 1979; Polyachenok and Novikov, 1963b,c; Spedding and Daane, 1960) and EuCl₂ (Da Silva et al., 2001; Goryushkin, 1996; Kapfenberger, 1938; Koyama et al., 1997; Kulagin and Laptev, 1976; Laptev et al., 1975) shows that three of a total of five measurements of the enthalpy of the $\beta \rightarrow \alpha$ transition for EuCl₂ gave fairly low values: 14.7 ± 3.0 kJ/mol (Goryushkin, 1996), 10.55 kJ/mol (Koyama et al., 1997), and 11.5 kJ/mol (Da Silva et al., 2001). These enthalpies are all lower than the enthalpies of melting: 16.0 ± 3.2 kJ/mol (Goryushkin, 1996), 11.05 kJ/mol (Koyama et al., 1997), and 18.7 kJ/mol (Da Silva et al., 2001). This was a determining argument for the selection of the 15.1 ± 1.7 kJ/mol value obtained by Laptev (1996) at 1043 ± 4 K as the enthalpy of the $\beta \rightarrow \alpha$ transition for SmCl₂, although other authors propose $\Delta_{tr}H^{\circ} = 25.0 \pm 5.0$ kJ/mol and $T_{tr} = 1045.7 \pm 3.0$ K (Goryushkin, 1996; Laptev et al., 1976b).

As for the melting point of SmCl₂, the available values, 1121 K (Spedding and Daane, 1960), 1132 K (Laptev, 1996; Polyachenok and Novikov, 1963b,c), 1131 \pm 2 K (Laptev et al., 1979), and 1128.8 \pm 2.0 K (Laptev et al., 1976b; Goryushkin, 1996), fall within a fairly narrow interval, which allowed us to recommend the value $T_{\rm m} = 1132$ K. We selected the 24.0 \pm 4.8 kJ/mol value from Laptev et al. (1976a,b) and Goryushkin (1996) as the enthalpy of melting of SmCl₂, although a value of 14.2 kJ/mol was reported in Laptev (1996) and Laptev et al. (1979). If the thermochemical constants for the phase transitions in SmCl₂ are selected as specified above, the total entropy $(\Delta_{tr}S^{\circ} + \Delta_{m}S^{\circ})$ is 35.68 J/(mol·K), which is larger by ~4 J/(mol·K) than the $\Delta_m S^\circ$ values for TmCl₂ and YbCl₂. This corresponds with the correlation between this parameter and the crystal structure type. The selection of the $\Delta_m H^\circ$ values from Laptev et al. (1979) and Laptev (1996) would be unreasonable because the $(\Delta_{tr}S^{\circ} + \Delta_{m}S^{\circ})$ value would then be lower than $\Delta_{m}S^{\circ}$ for TmCl₂ and YbCl₂.

We can expect that the $(\Delta_{tr}S^{\circ} + \Delta_mS^{\circ})$ value for EuCl₂ should be close to that for SmCl₂. Apart from the enthalpies of $\beta \rightarrow \alpha$ transition for EuCl₂ mentioned above (Da Silva et al., 2001; Goryushkin, 1996; Koyama et al., 1997), there is a value of 20.5 \pm 0.8 kJ/mol measured by Laptev (1996) at 1020 ± 4.0 K. The data from Da Silva et al (2001), Goryushkin (1996), and Koyama et al. (1997) were obtained at 1014, 1022.4 ± 3.8, and 1016.8 K, respectively. Weighted averaging of both the temperatures and enthalpies of the $\beta \rightarrow \alpha$ phase transition from these four works yields $T_{\rm tr} = 1020 \pm 8$ K and $\Delta_{\rm tr} H^{\circ} = 15.2 \pm 9.2$ kJ/mol. The averaging of the melting points, \approx 1123 K (Kapfenberger, 1938), 1127 \pm 2 K (Laptev et al., 1975; Kulagin and Laptev, 1976), 1134.4 ± 4.7 K (Goryushkin, 1996), 1123.9 K (Koyama et al., 1997), 1125 K (Da Silva et al., 2001), and 1127 \pm 2.0 K (Laptev, 1996) gives $T_{\rm m} = 1127 \pm 8$ K. At such averaged $\Delta_{tr}H^{\circ}$, T_{tr} , and T_{m} values, comparable ($\Delta_{tr}S^{\circ} + \Delta_{m}S^{\circ}$) values for SmCl₂ and EuCl₂ can be obtained if we assume that the enthalpy of melting is 23.0 ± 1.3 kJ/mol (see Kulagin and Laptev, 1976; Laptev, 1996; Laptev et al., 1975). We then obtain $(\Delta_{tr}S^{\circ} + \Delta_mS^{\circ}) = 35.31 \text{ J/(mol}\cdot\text{K})$. Calculation of the total enthalpy from the four values obtained in one measurement yields results either above or below this value because, the spread of the $\Delta_{tr}H^{\circ}$ values being fairly large, $\Delta_{m}H^{\circ}$ values range over a broader interval: 23.0 ± 1.3 kJ/mol (Kulagin and Laptev, 1976; Laptev, 1996; Laptev et al., 1975), 16.0 ± 3.2 kJ/mol (Goryushkin, 1996), 11.05 kJ/mol (Koyama et al., 1997), and 18.7 kJ/mol (Da Silva et al., 2001).

To summarize, the data available presently can be used to reliably select the temperatures and enthalpies of phase transitions for only four lanthanide dichlorides, SmCl₂, EuCl₂, TmCl₂, and YbCl₂ (see Table 59). The expected values of these parameters for the other lanthanide dichlorides can be estimated using the correlation mentioned above for the

	T _m	$\Delta_{\sf m} {\it H}^{\circ}$	$ {C}_{exs}(T_m)$	C _p (liq)
R	(К)	(kJ∕mol)	(J∕(mol∙K))	
La	1070	38.0	4.95	113.6
Ce	1080	38.3	10.26	118.2
Pr	1090	38.7	7.07	114.4
Nd	1098	39.0	7.81	114.9
Pm	1110	39.4	9.62	116.2
Sm ^a	1132	24.0	9.39	115.6
Eu ^a	1127	23.0	0.00	105.8
Gd	1143	40.6	6.86	113.4
Tb	1113	35.0	3.08	110.9
Dy	1086	34.1	1.20	110.0
Но	1059	33.3	0.45	108.7
Er	1031	32.4	0.35	108.0
Tm	991	31.1	0.11	107.3
Yb	987	31.1	0.00	106.5
Lu	949	29.8	0.24	106.4

TABLE 59 Temperatures, enthalpies of phase transitions, heat capacities of the α -polymorphs and liquid state, and excess contributions to heat capacities at the melting temperatures of lanthanide dichlorides

^{*a*} For Sm and Eu, $T_{tr} = 1043$ and 1020 K, $\Delta_{tr}H^{\circ} = 15.1$ and 15.2 kJ/mol, and $C_{p}^{\circ}(\alpha-RCl_{2}) = 128.2$ and 118.8 J/(mol K), respectively.

entropy of the phase transition and by comparing the temperatures of melting of RCl₃ and RCl₂.

Indeed, it follows from an analysis of the T_m values recommended for lanthanide trichlorides that the dependence of these values on the atomic number of lanthanides (see Figure 35) has a somewhat asymmetric Vshaped form with a minimum at TbCl₃ (Chervonnyi and Chervonnaya, 2007b). Approximation of the T_m values in the RCl₃ series with R = La–Tb and R = Tb–Lu by straight lines gives values that differ within ±10 K from those recommended in (Chervonnyi and Chervonnaya, 2007b). A similar dependence for the RCl₂ series with R = La–Gd, however in the opposite direction, can be constructed for lanthanide dichlorides using the data on NdCl₂ from Goryushkin et al. (1991) and those for SmCl₂, and EuCl₂ listed in Table 59. For the series of RCl₂ with R = Tb–Lu, such a dependence can also be obtained with the data on GdCl₂, TmCl₂, and YbCl₂ collected in Table 59.

The estimated enthalpies of melting of RCl₂ (R = La–Pm, Gd) were found from the entropy of melting taken to be 35.50 J/(mol·K), this being the mean ($\Delta_{tr}S^{\circ} + \Delta_{m}S^{\circ}$) value for SmCl₂ and EuCl₂. As concerns $\Delta_{m}H^{\circ}$



FIGURE 35 Melting points of lanthanide di- and trichlorides: Δ , temperatures of melting of RCl₃ recommended in Chervonnyi and Chervonnaya (2007b); •, temperatures of melting of RCl₂ selected from the literature data; and 0, our present estimates for RCl₂. Reproduced from Chervonnyi and Chervonnaya (2008a) with permission from Pleiades Publishing, Ltd.

for RCl₂ with R = Tb-Er, Lu, these values were estimated using the entropy value 31.44 J/(mol·K), which is the mean value for TmCl₂ and YbCl₂.

9.2.4 Estimation of the heat capacity of $\alpha\text{-SmCl}_2\text{, }\alpha\text{-EuCl}_2\text{, and RCl}_2$ in liquid state

According to the measurement results obtained by Da Silva et al. (2001) and reported on Figure 34, the heat capacity of α -EuCl₂ is described by the polynomial

$$C_{\rm p}^{\rm o}(\alpha - {\rm EuCl}_2, T) = 6748.2 - 12.26T + 5.6621 \times 10^{-3}T^2$$

It decreases from 138.31 to 111.69 J/(mol·K) over the temperature range 1014–1125 K. In our view, this dependence does not correspond to real changes in the heat capacity of this polymorph. Indeed, according to the database (IVTANTERMO, 2004), the heat capacity of α -BaCl₂ is constant over the whole temperature range of its existence. Accordingly, we assumed that the heat capacity of α -EuCl₂ amounts to 118.8 J/(mol·K); this value was obtained by averaging the experimental data from Da Silva et al. (2001) and used as a reference value for estimating the heat capacity is 9.4 J/(mol·K) for α -SmCl₂ and zero for α -EuCl₂, the heat capacity of the

former should be higher than that of the latter by approximately this value. This gives $C_p^{\circ}(\alpha-\text{SmCl}_2) = 128.2 \text{ J/(mol}\cdot\text{K})$ over the temperature range of the existence of α -SmCl₂.

The absence of data on the heat capacity of lanthanide dichlorides in the liquid state makes us use approximate estimation methods. We applied the Neumann–Kopp rule of summation, according to which the heat capacity C_p° of a compound can be calculated from the weighted component contributions constituting it. Considering the formation of RCl₂ from R and RCl₃, we find that

$$C_{\rm p}^{\circ}({\rm RCl}_2) = \frac{1}{3}C_{\rm p}^{\circ}({\rm R}) + \frac{2}{3}C_{\rm p}^{\circ}({\rm RCl}_3).$$
 (30)

In particular, the Neumann–Kopp rule was applied in this form by Da Silva et al. (2001) to check if the heat capacity of EuCl₂ was correctly determined over the temperature range 400–900 K. The calculated values were found to be higher than the experimental values by $\sim 6\%$.

We suppose that Eq. (30) can be applied to estimate the heat capacities of liquids, but for a limited number of lanthanide dichlorides only. We used this equation to estimate $C_p^{\circ}(\text{EuCl}_2, \text{liq})$ and $C_p^{\circ}(\text{YbCl}_2, \text{liq})$. These substances were selected because there is no excess contribution to the heat capacities of the lanthanides themselves (see Martin et al., 1978) and their dichlorides (see Table 7). The calculated $C_p^{\circ}(\text{EuCl}_2, \text{liq})$ and $C_p^{\circ}(\text{YbCl}_2, \text{liq})$ values were 105.8 and 106.5 J/(mol·K), respectively. These data were obtained using the heat capacities of europium and ytterbium from the database (IVTANTERMO, 2004) and the lattice heat capacity components $C_{\text{lat}}^{\circ}(\text{liq})$ from Chervonnyi and Chervonnaya (2007b) as the heat capacities of europium and ytterbium trichlorides.

It follows from numerous studies of the melt structure of lanthanide trihalides and their mixtures with alkali-metal halides that this structure is a peculiar sparse lattice comprising separate layers with weak interlayer interactions between distorted octahedra. This allows us to treat the heat capacities of RF₃ and RCl₃ melts as the sums of the lattice contributions of the liquids $C_{lat}^{\circ}(liq)$ and excess heat capacities $C_{exs}^{\circ}(T_m)$. Chervonnyi and Chervonnaya (2007b) demonstrated that the experimental $C_p^{\circ}(RX_3, liq)$ values (X = F, Cl) minus excess heat capacity contributions calculated by the classical scheme for the temperature corresponding to the melting point can be represented as linear functions of the polarizing action of the cation *e/r*, where *e* is the charge of the cation and *r* is its radius.

We assumed that the same rule should hold for lanthanide dichlorides. Although data on the structure of the corresponding melts are absent, there exist a fairly large number of theoretical and experimental studies of group II metal dichlorides (Biggin and Enderby, 1981a,b; Edwards et al., 1978; Fukushina et al., 2001; Gray-Weale et al., 2000; McGreevy and Mitchell, 1982; Okamoto et al., 2002a; Pavlatou et al., 1997; Ribeiro et al., 1998, 1999; Shirao et al., 2002; Wilson, 2003; Wilson and Madden, 1993, 1994, 1997; Wilson and Ribeiro, 1999; Yannopoulos et al., 2003). According to these data, their melting results in the formation of a similar sparse network, whose main structural elements are $(MX_4)^{2-}$ tetrahedra.

The $C_{p}^{\circ}(\text{RCl}_{2}, \text{lig})$ estimates for europium and ytterbium dichlorides obtained using the Neumann-Kopp rule of summation can virtually be used as $C_{lat}(liq)$ reference values for determining this characteristic for the other lanthanide dichlorides with different crystal structure types. According to Shannon (1976), the radii of lanthanide cations with different CNs show parallel dependences on the atomic number of R, and the $C_{lat}(RCl_3, liq) - C_{lat}(RCl_2, liq)$ difference of lattice contributions can be considered as constant among lanthanide tri- and dichlorides. For the structures characterized by a higher CN, this difference is determined by the $C_{lat}(liq)$ values for EuCl₃ and EuCl₂, and for the structures with a lower CN, by the $C_{lat}^{\circ}(liq)$ values for YbCl₃ and YbCl₂, especially because, in spite of the use of the Neumann–Kopp rule, the $C_{lat}^{\circ}(liq)$ value for EuCl₂ is lower than that for YbCl₂; the same trend is observed for EuCl₃ and YbCl₃ (Chervonnyi and Chervonnaya, 2007b). This approach allowed us to calculate the lattice contributions to the heat capacities of melts for all the lanthanide dichlorides. The sums of the lattice and excess contributions calculated by the classical scheme for $T = T_m$ with the use of the data from Table 7 gives the heat capacities of RCl₂ in the liquid state listed in Table 59.

The lattice contributions to the heat capacities of molten $GdCl_2$ and $TbCl_2$ were obtained on the assumption of their linear dependence upon the ionic radius. This estimate was made because it was accepted in this work that gadolinium and terbium dihalides have $SrBr_2$ -type structures with CN = 8. The smoothed crystal radii of Eu^{2+} , Gd^{2+} , Tb^{2+} , and Dy^{2+} used in our calculations were taken from Chervonnyi and Chervonnaya (2005c).

9.2.5 Thermodynamic functions

The thermochemical parameters described above were used to calculate the temperature dependence of the reduced Gibbs energy in the form of the traditional polynomial. The procedure of calculations is described in Section 4. The resulting thermodynamic functions are presented in Table A8 in the form of the f_i coefficients (see Appendix).

Our analysis of the initial thermochemical parameter values used in thermodynamic function calculations gives a temperature dependence of the $-[G^{\circ}(T) - H^{\circ}(298)]/T$ parameter different from the data that we used for calculating the enthalpies of sublimation of SmCl₂ (Chervonnyi and Chervonnaya, 2004e), EuCl₂ (Chervonnyi and Chervonnaya, 2004a, 2005b), and YbCl₂ (Chervonnyi and Chervonnaya, 2004f). Since the S° (298) values used in the present work remained unchanged, the reduced

Gibbs energy values at standard temperature were the same as those reported in Chervonnyi and Chervonnaya (2004a,e,f, 2005b). Differences appear as the temperature increases and reach 1.5, 1.7, and 0.1 J/(mol·K) at $T_{\rm m}$ for SmCl₂, EuCl₂, and YbCl₂, respectively. These differences are mainly caused by variation of $C_{\rm p}^{\circ}(T)$ values over the temperature interval 298 K < $T < T_{\rm m}$.

This circumstance also results in different $H^{\circ}(T) - H^{\circ}(298)$ values used in calculations of the enthalpies of sublimation at standard temperature by the second law of thermodynamics. Enthalpy deviations are also influenced by corrections to the enthalpies of phase transitions. For this reason, the differences in $H^{\circ}(T) - H^{\circ}(298)$ between data in Chervonnyi and Chervonnaya (2004a,e,f, 2005b) and this work are more noticeable. In particular, at $T_{\rm m}$, they amount to 3.3, 5.8, 10.1, and 0.5 kJ/mol for SmCl₂, α -EuCl₂, EuCl₂(liq), and YbCl₂, respectively.

A comparison of the results obtained with those reported by Barin (1995) can only be done for YbCl₂. The differences in the $H^{\circ}(T) - H^{\circ}(298)$ and $- [G^{\circ}(T) - H^{\circ}(298)]/T$ values over the temperature range 298.15–900 K amount to ~5–8% and ~7–8%, respectively.

9.3 Sublimation enthalpies

The enthalpies of sublimation under standard conditions were calculated according to the second and third laws of thermodynamics from the experimental saturated vapor pressures (Chervonnyi and Chervonnaya, 2004a,e,f, 2005b). In calculations by the second law, the $\Delta_{sub}H^{\circ}(T)$ value was determined from the slope of a semilogarithmic plot, and *T* was set equal to the mean temperature of measurements. These data were then used to calculate the enthalpies of atomization. Next, the sequence of these values was analyzed, which was much broader because of the introduction of additional data obtained from equilibrium constant measurements for gas-phase reactions in the R + MCl₂ systems and from appearance energies AE(R⁺/RCl₂).

This approach was found to be very fruitful. Using it, we were able to reveal inconsistency of the experimental data on several thermodynamic parameters. This in the first place concerns the available data on the low-temperature heat capacities of the substances under consideration in the condensed state and the standard entropies calculated from these values. In addition, this approach gave us the possibility of selecting suitable enthalpies of formation for crystalline compounds, $\Delta_{\rm f} H^{\circ}({\rm RCl}_2, {\rm cr}, 298)$, under standard conditions. Finally, this allowed us to determine the recommended enthalpies of sublimation of SmCl₂, EuCl₂, and YbCl₂.

This procedure, however, becomes ineffective when applied to the other lanthanide dichlorides. Saturated vapor pressure measurements, which can directly be used to calculate the enthalpies of sublimation according to the second and third laws, are only reported for SmCl₂, EuCl₂, and YbCl₂ among lanthanide dichlorides (saturated vapor pressure measurements for NdCl₂ (Kudin et al., 1993b) are considered below!). The available experimental equilibrium constants (Chervonnyi, 1977a; Chervonnyi and Chervonnaya, 2004a,b,e,f, 2005b) and appearance energies (Sapegin, 1984; Sapegin et al., 1982a,b, 1984) can be used to determine the enthalpies of atomization for almost all the dichlorides (except PmCl₂), but it is difficult to evaluate the reliability of these data.

Usually, trends in $\Delta_{at}H^{\circ}(298)$ variations depending on the atomic numbers of lanthanides are considered. This dependence, however, has the form of a broken line with maxima at lanthanum, gadolinium, and lutetium and minima at europium and ytterbium. In addition, an increase in $\Delta_{at}H^{\circ}(298)$ is usually observed when going from dysprosium to erbium compounds. A smoother dependence on the atomic number of lanthanides was obtained for the enthalpies of sublimation of lanthanide trifluorides and trichlorides. We believe that the use of this feature allows $\Delta_{sub}H^{\circ}(298)$ values to be predicted more accurately for separate lanthanide dichlorides. Accordingly, the reliability of all the thermodynamic data can then be estimated.

The enthalpies of sublimation under standard conditions calculated from the saturated vapor pressures (Chervonnyi and Chervonnaya, 2004a,e,f, 2005b; Chervonnyi et al., 1973; Frid et al., 1964; Hariharan and Eick, 1972; Hariharan et al., 1972; Hastie et al., 1968; Il'in et al., 1973; Khasanshin et al., 1998; Kudin et al., 1997b; Kuznetsov et al., 1997b; Pogrebnoi and Kudin, 2003a,b; Polyachenok and Novikov, 1963d) are listed in Table 60.

Table 61 contains the enthalpies of sublimation calculated from the enthalpies of atomization. The latter were in turn determined on the basis of the equilibrium constants $K_p^{\circ}(T)$ of gas-phase reactions obtained during the vaporization of R + MCl₂ mixtures (M = Ba, Eu) under Knudsen conditions (Chervonnyi, 1977a; Chervonnyi and Chervonnaya, 2004a,b, e,f, 2005b) and the appearance energies AE(R⁺/RCl₂) (Chervonnyi and Chervonnaya, 2004a,e,f; Hariharan et al., 1972; Hastie et al., 1968; Sapegin, 1984; Sapegin et al., 1982a,b, 1984). The $\Delta_f H^{\circ}$ (cr, 298) values used in these calculations were described in Section 8. The necessary additional characteristics were selected as follows.

The $\Delta_{at}H^{\circ}(RCl_2, 298)$ values were calculated from the equilibrium constants of gas-phase reactions using the thermodynamic functions of gaseous BaCl₂, Ba, and R from the IVTANTERMO database (2004). The thermodynamic functions of gaseous lanthanide mono- and dichlorides were taken from Chervonnyi and Chervonnaya (2003, 2004c,d, 2007d,e).

In these calculations, $\Delta_{at}H^{\circ}$ (BaCl₂, 298) and $\Delta_{at}H^{\circ}$ (BaCl, 298) were taken to be 926.905 and 442.592 kJ/mol, respectively (see IVTANTERMO, 2004).

	II law	II law		III law				
R	β ^a	α ^b	liq ^c	β ^a	α ^b	liq ^c	References	$\Delta_{sub} \mathcal{H}^{\circ}$ (298) ^d
Sm	_	_	331.5	_	_	335.0	Polyachenok and Novikov (1963d)	338.7 ± 2.5
	_	_	331.2	-	_	339.9	Frid et al. (1964)	
	_	321.4	315.1	_	_	_	Chervonnyi et al. (1973)	
	266.6	257.8	368.5	330.6	334.8	336.6	Il'in et al. (1973)	
	_	345.0	338.8	-	_	-	Chervonnyi et al. (1975)	
	-	329.0	343.9	-	341.2	341.6	Kuznetsov et al. (1999) and Khasanshin et al. (1998)	
	_	312.1	321.2	-	337.7	338.5	Pogrebnoi and Kudin (2003a)	
	_	_	343.5	-	_	338.2	Chervonnyi and Chervonnaya (2004e)	
Eu	_	_	330.3	-	_	350.5	Polyachenok and Novikov (1963d)	343.7 ± 1.8
	_	_	324.2	-	_	_	Hastie et al. (1968)	
	_	_	370.0	-	_	357.9	Hariharan and Eick (1972)	
	_	_	330.2	-	_	_	Chervonnyi et al. (1973)	
	-	-	332.9	-	-	-	Chervonnyi et al. (1973)	
	369.5	289.0	_	338.2	336.7	-	Chervonnyi and Chervonnaya (2004a) and Il'in et al. (1973)	
	_	_	349.3	-	_	_	Chervonnyi et al. (1975)	
	-	-	357.0	-	-	-	Chervonnyi et al. (1975)	
	-	-	346.2	-	-	345.3	Pogrebnoi and Kudin (2003b)	
	_	361.6	373.0	-	352.9	349.8	Pelipets et al. (2003)	

TABLE 60 Enthalpies of sublimation RCl_2 ($\Delta_{sub}H^{\circ}(298)$, kJ/mol) calculated according to the second and third laws of thermodynamics

Yb	-	-	322.6	-	-	328.2	Polyachenok and Novikov (1963d)	326.4 ± 3.2
	-	-	337.0	-	-	334.7	Frid et al. (1964)	
	-	-	364.3	-	-	342.8	Hariharan et al. (1972)	
	-	281.0	308.2	-	324.0	328.0	Il'in et al. (1973)	
	-	-	335.4	-	-	-	Chervonnyi et al. (1975)	
	-	-	365.9	-	-	337.2	Kuznetsov et al. (1997b)	
	-	-	364.3	-	-	339.1	Kudin et al. (1997b)	
	-	-	359.3	-	-	337.5	Pogrebnoi and Kudin (2003a)	
	-	-	310.9	-	-	330.0	Chervonnyi and Chervonnaya (2004f)	

^{*a*} Calculations were performed using vapor pressures over the β phase. ^{*b*} Calculations were performed using vapor pressures over the α phase. ^{*c*} Calculations were performed using vapor pressures over the melt. ^{*d*} The Δ_{sub}*H*°(298) values calculated from the enthalpies of atomization recommended by Chervonnyi and Chervonnaya (2004a,e,f, 2005b).

	$\Delta_{ m sub}{\cal H}^{\circ}$ (298) values calculated from								
R	κ _p (T) measu	rements for R $+$	AE(R ⁺ /RCl ₂) measurements						
	MCl ₂		а	Ь					
La	BaCl ₂	175.1 ^c	-	189.8	-				
Ce	$BaCl_2$	263.4^{d}	235.0	234.8	_				
Pr	$BaCl_2$	331.4 ^d	312.1	319.6	_				
Nd	$BaCl_2$	328.4 ^d	337.2	332.8	_				
	EuCl ₂	346.0^{d}	338.2	_	_				
Pm	_	_	_	_	_				
Sm	$BaCl_2$	339.6 ^d	_	358.1	343.6 ^e				
	$BaCl_2$	338.5 ^e	_	_	_				
Eu	$BaCl_2$	342.2^{d}	_	352.9	338.5 ^f				
	$BaCl_2$	346.7 ⁸	_	_	348.1 ⁸				
Gd	EuCl ₂	193.3 ^d	214.7	174.0	_				
Tb	$BaCl_2$	290.1 ^d	293.2	282.8	_				
Dy	$BaCl_2$	332.9 ^d	326.3	323.0	_				
•	EuCl ₂	328.4 ^d	327.0	_	_				
Но	$BaCl_2$	311.3 ^d	303.9	303.1	_				
Er	$BaCl_2$	282.4^{d}	278.5	_	_				
Tm	$BaCl_2$	321.6 ^d	_	319.0	_				
	EuCl ₂	325.5 ^d	_	_	_				
Yb	$BaCl_2$	321.4 ^d	_	338.5	324.0 ^h				
	$BaCl_2$	327.3 ⁱ	_	-	328.8 ⁱ				
Lu	BaCl ₂	157.8 ^d	149.7	-	-				

TABLE 61 $\Delta_{sub}H^{\circ}(298)$ values for RCl₂ (kJ/mol)

 $^{a}_{sub}H^{\circ}(298)$ values obtained from averaged mass spectra of lanthanide tri- and dichlorides.

^b Values calculated from AE(R⁺/RCl₂) measurements (Sapegin, 1984; Sapegin et al., 1982a,b, 1984).

^c Chervonnyi and Chervonnaya (2004b).

^d Chervonnyi (1977a).

^e Chervonnyi and Chervonnaya (2004e).

^f Hastie et al. (1968).

^g Chervonnyi and Chervonnaya (2004a, 2005b).

^h Hariharan et al. (1972).

ⁱ Chervonnyi and Chervonnaya (2004f).

The enthalpy of atomization of $EuCl_2$ was set equal to 899.3 kJ/mol (Chervonnyi and Chervonnaya, 2004a, 2005b).

The enthalpies of atomization were calculated from the appearance energies $AE(R^+/RCl_2)$ using the ionization energies of lanthanides recommended by the National Institute of Standards (USA) (NIST Ground Levels). Their recalculation from 0 to 298 K and calculations of $\Delta_{sub}H^{\circ}(298)$ from the enthalpies of atomization (see Table 61) were

performed using the necessary auxiliary characteristics (Chervonnyi and Chervonnaya, 2003, 2004c,d, 2007d,e; IVTANTERMO, 2004).

Two series of values for the enthalpies of sublimation are given in Table 61 for the R + MCl₂ systems (R = Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu). The data from the first series were calculated using $K_{p}^{\circ}(T)$ from Chervonnyi (1977a). The second series was obtained by processing the experimental data from Chervonnyi (1977a) with the use of averaged mass spectra of lanthanide tri- and dichlorides. This procedure was described in detail in Section 6. In our view, the corrections introduced in this way into calculations of equilibrium constants for reactions with the participation of RCl₂ increase the reliability of the results.

As an argument in favor of the reliability of the thermodynamic functions of the condensed state, consider the enthalpies of sublimation of $SmCl_2$, $EuCl_2$, and $YbCl_2$ (see Table 60).

The thermodynamic functions described in this work were used to process saturated vapor pressure values over a very broad temperature range (from ~900 to ~1700 K), in which these dichlorides exist in the solid state (α and β polymorphs) and as melts. In spite of the complexity of their behavior at high temperatures, the enthalpies of sublimation calculated according to the third law of thermodynamics lie within fairly narrow ranges, of ± 5.5 kJ/mol for SmCl₂, ± 10.6 kJ/mol for EuCl₂, and ± 9.4 kJ/mol for YbCl₂.

Note that if the exaggerated $\Delta_{sub}H^{\circ}(298)$ values obtained from the experimental data reported by Hariharan et al. (1972) and Hariharan and Eick (1972) are excluded, the intervals specified above become still narrower for EuCl₂ and YbCl₂. No temperature dependence is observed for the enthalpies of sublimation of these compounds, which is evidence of the absence of systematic errors in their thermodynamic functions.

The refinement of the thermodynamic functions for SmCl₂, EuCl₂, and YbCl₂ compared with those reported in Chervonnyi and Chervonnaya (2004a,e,f, 2005b) narrowed the spread of the enthalpies of sublimation found using the second and third laws of thermodynamics from saturated vapor pressures; this is particularly noticeable for Sm and Eu. The enthalpies of sublimation found by the third law, which were as a rule higher than the recommended values, decreased.

For EuCl₂, the mean $\Delta_{sub}H^{\circ}(298)$ value is 344.2 \pm 2.3 kJ/mol, exluding data from Hariharan and Eick (1972). It is higher than that obtained by Chervonnyi and Chervonnaya (2004a, 2005b) on the basis of the enthalpies of atomization by only 0.5 kJ/mol. The reliability of the $\Delta_{at}H^{\circ}(EuCl_2, 298)$ value is substantiated by the agreement within 1 kJ/mol of two (of a total of three) enthalpies of sublimation determined in studies of the Nd + BaCl₂, Nd + EuCl₂, Dy + BaCl₂, and Dy + EuCl₂ gas-phase reactions (see Table 61). Only in the third case, the difference of the enthalpies of sublimation determined in studies of the Tm + BaCl₂ and Tm + EuCl₂

gas-phase reactions is larger, amounting to 3.8 kJ/mol. Bearing this in mind, we believe that there are no sufficient grounds for reconsidering the enthalpies of atomization and sublimation of europium dichloride recommended by Chervonnyi and Chervonnaya (2004a, 2005b) on the basis of the thermodynamic functions calculated in this work from the data of Chervonnyi and Chervonnaya (2008a).

The $\Delta_{at}H^{\circ}(\text{SmCl}_2, 298)$ value recommended by Chervonnyi and Chervonnaya (2004e) for SmCl₂ is 912.0 ± 4.0 kJ/mol. It was virtually predetermined by the mean enthalpy of sublimation found by the third law (338.7 ± 0.5 kJ/mol) with the accepted $\Delta_f H^{\circ}(\text{SmCl}_2, \text{cr}, 298) = -802.5 \pm 2.2 \text{ kJ/mol}$ value (Morss, 1976). Enthalpies of atomization close to the above value are obtained from the $K_p^{\circ}(T)$ values found for the Sm + BaCl₂ system, 910.7 ± 10 kJ/mol (Chervonnyi, 1977a) and 911.8 ± 1.8 kJ/mol (Chervonnyi and Chervonnaya, 2004e). Calculations from the AE(Sm⁺/SmCl₂) give 907.1 ± 10 kJ/mol (Chervonnyi and Chervonnaya, 2004e).

The AE(R⁺/RCl₂) values were not experimentally determined in Chervonnyi and Chervonnaya (2004e,f). They were found according to the equation $AE(R^+/RCl_2) = AE(R^+/RCl_3) + AE(RCl^+/RCl_2) - AE(RCl^+/RCl_3)$ from the appearance energies of the R⁺ and RCl⁺ ions in the ionization of RCl₃ measured in these works and the appearance energy of RCl⁺ in the ionization of RCl₂; both AE(Sm⁺/SmCl₂) and AE(Yb⁺/YbCl₂) are equal to 15.0 \pm 0.1 eV.

Because of the refinement of the thermodynamic functions of SmCl₂ (Chervonnyi and Chervonnaya, 2008a), the enthalpies of sublimation had to be recalculated using new data (Chervonnyi and Chervonnaya, 2004e, 2008a). An error was found in calculations of the enthalpy of sublimation by the third law from saturated vapor pressures over the melt. This error distorted average value of $\Delta_{\rm sub}H^{\circ}$ (SmCl₂, 298) reported in Chervonnyi and Chervonnaya (2004e). In reality, the use of the coefficients of the polynomial that describes the reduced Gibbs energy of liquid samarium dichloride (Chervonnyi and Chervonnaya, 2004e) yields a mean $\Delta_{\rm sub}H^{\circ}$ (SmCl₂, 298) value equal to 340.7 \pm 1.0 kJ/mol.

Nevertheless, calculations of the mean enthalpy of sublimation of SmCl₂ from the data presented in Table 60 only taking into account the results of measurements for which the difference between second and third law calculations does not exceed 10 kJ/mol yield 338.7 ± 2.5 kJ/mol. This value agrees, within the error specified, with those found by measuring the equilibrium constant for the gas-phase reaction in the Sm + BaCl₂ system, 339.6 kJ/mol (Chervonnyi, 1977a) and 338.5 kJ/mol (Chervonnyi and Chervonnaya, 2004e). The difference between this value and the results of AE(Sm⁺/SmCl₂) measurements is somewhat larger (see Table 61). The enthalpies of sublimation of SmCl₂ given in Table 61 were obtained using the $\Delta_f H^{\circ}$ (SmCl₂, cr, 298) value

from Morss (1976), -802.5 ± 2.2 kJ/mol, although the scheme described in Section 8 yields a negligibly different value of -802.076 kJ/mol.

The enthalpy of sublimation of YbCl₂ was determined in Chervonnyi and Chervonnaya (2004f) by comparing the $\Delta_{at}H^{\circ}(298)$ values obtained from saturated vapor pressure measurements over solid and liquid samples, equilibrium constants of gas-phase reactions in the Yb + BaCl₂ system, and appearance energies $AE(Yb^+/YbCl_2)$. The enthalpy of atomization found in this way (850.7 \pm 2.8 kJ/mol) finally gave $\Delta_{sub}H^{\circ}$ $(YbCl_2, 298) = 326.4 \pm 2.5 \text{ kJ/mol}$. We had to disregard several results of saturated vapor pressure measurements (Hariharan et al., 1972; Kudin et al., 1997b; Kuznetsov et al., 1997b; Pogrebnoi and Kudin, 2003a) because the enthalpy of sublimation found from them according to the second law of thermodynamics was substantially higher than the value calculated by the third law. This cannot be characteristic of compounds that are prone to experience disproportionation. Note that the $\Delta_{sub}H^{\circ}$ (298, III law) values from Hariharan et al. (1972), Kudin et al. (1997b), Kuznetsov et al. (1997b), and Pogrebnoi and Kudin (2003a) are close to those found from AE(Yb⁺/YbCl₂) values (Sapegin, 1984; Sapegin et al., 1982a). Another group of measurements, including saturated vapor pressure (Chervonnyi and Chervonnaya, 2004f; Frid et al., 1964; Il'in et al., 1973; Polyachenok and Novikov, 1963d), equilibrium constant (Chervonnyi, 1977a; Chervonnyi and Chervonnaya, 2004f), and appearance energy (Chervonnyi and Chervonnaya, 2004f; Hariharan et al., 1972) measurements, give $\Delta_{sub}H^{\circ}(298)$ enthalpies grouped about a value lower by ~10 kJ/mol than $\Delta_{sub}H^{\circ}(298)$ from Hariharan et al. (1972), Kudin et al. (1997b), Kuznetsov et al. (1997b), and Pogrebnoi and Kudin (2003a).

The refinements introduced by Chervonnyi and Chervonnaya (2008a) into the thermodynamic functions of ytterbium dichloride insignificantly influenced their values. The mean enthalpy of sublimation calculated by the third law of thermodynamics (see Table 61) increased by as little as 0.5 kJ/mol. The trend toward an increase in $\Delta_{\text{sub}}H^{\circ}(298, \text{ II law})$ compared with the $\Delta_{\text{sub}}H^{\circ}(298, \text{ III law})$ values calculated from the data reported in Hariharan et al. (1972), Kudin et al. (1997b), Kuznetsov et al. (1997b), and Pogrebnoi and Kudin (2003a), however, becomes more noticeable. Conversely, in processing the results obtained by II'in et al. (1973), Polyachenok and Novikov (1963d), Frid et al. (1964), and Chervonnyi and Chervonnaya (2004f), the convergence of the $\Delta_{\text{sub}}H^{\circ}(298, \text{ II law})$ and $\Delta_{\text{sub}}H^{\circ}(298, \text{ II law})$ values becomes closer.

It follows that the mean enthalpy of sublimation found from saturated vapor pressure measurements (Chervonnyi and Chervonnaya, 2004f; Frid et al., 1964; Il'in et al., 1973; Polyachenok and Novikov, 1963d) is 329.0 kJ/mol. It is smaller than the value obtained from ionization data (Chervonnyi and Chervonnaya, 2004f) by only 0.2 kJ/mol and larger by 1.7 kJ/mol than that determined from equilibrium constant

measurements for the gas-phase reaction in the Yb + BaCl₂ system (Chervonnyi and Chervonnaya, 2004f). It is therefore reasonable to correct the $\Delta_{sub}H^{\circ}$ (YbCl₂, 298) value recommended by Chervonnyi and Chervonnaya (2004f) and to set it equal to 328.4 \pm 2.5 kJ/mol.

It follows from the above discussion that the thermodynamic functions of compounds in the condensed state, verified for three examples only (SmCl₂, EuCl₂, and YbCl₂), are fairly reliable in spite of extensive use of various correlations for their determination. We were able to obtain data that allowed thermodynamic calculations for high temperatures to be performed with acceptable accuracy (Chervonnyi and Chervonnaya, 2008a). Judging from the convergence of the enthalpies of sublimation obtained in processing experimental data by various methods, these functions involve errors of \sim 2–3 J/(mol·K) at temperatures close to the melting points of pure compounds.

The selection of the recommended $\Delta_{sub}H^{\circ}(298)$ values for the other lanthanide dichlorides is based on the use of values obtained from equilibrium constant and appearance energy measurements. It follows from Tables 61 and 62 that the recommended enthalpy of sublimation was derived from AE(Gd⁺/GdCl₂) measurements (Sapegin, 1984; Sapegin

$\Delta_{sub}H^{\circ}$	л Ц°	A			
(200)	⊿f⊓ ()	$\Delta_{at}H^{\circ}$		(10(- 0)	A (10/0)
(298)	(g, 298)	(298)	$\Delta_{sub}H^{\circ}(0)$	$\Delta_{\mathbf{f}}\mathbf{H}^{\circ}(\mathbf{g},0)$	$\Delta_{at} H^{\circ}(0)$
175.1	-326.632	999.236	176.468	-325.432	995.015
235.5	-320.473	980.151	236.964	-317.843	976.083
315.9	-353.737	952.154	317.269	-352.700	948.940
337.7	-355.198	924.931	339.045	-354.083	921.323
337.6	-417.371	919.138	338.920	-415.873	915.113
338.7	-463.376	911.577	339.944	-463.017	907.257
343.7	-480.500	899.291	344.936	-477.699	894.939
173.7	-315.709	956.824	175.226	-313.054	952.294
288.2	-310.258	938.918	290.047	-306.450	933.690
326.7	-361.738	889.594	328.921	-358.765	886.005
303.6	-360.580	903.375	305.774	-358.606	899.846
278.5	-362.122	918.553	280.633	-360.944	915.184
325.5	-386.234	861.597	327.594	-384.687	857.927
328.4	-453.600	848.690	330.475	-452.014	844.254
149.7	-281.362	951.828	151.700	-280.172	947.412
	(298) 175.1 235.5 315.9 337.7 337.6 338.7 343.7 173.7 288.2 326.7 303.6 278.5 325.5 328.4 149.7	$\begin{array}{c cccc} (298) & (g, 298) \\ \hline 175.1 & -326.632 \\ 235.5 & -320.473 \\ 315.9 & -353.737 \\ 337.7 & -355.198 \\ 337.6 & -417.371 \\ 338.7 & -463.376 \\ 343.7 & -463.376 \\ 343.7 & -480.500 \\ 173.7 & -315.709 \\ 288.2 & -310.258 \\ 326.7 & -361.738 \\ 303.6 & -360.580 \\ 278.5 & -362.122 \\ 325.5 & -386.234 \\ 328.4 & -453.600 \\ 149.7 & -281.362 \\ \end{array}$	$\begin{array}{c cccc} \hline (298) & (g, 298) & (298) \\ \hline (175.1 & -326.632 & 999.236 \\ 235.5 & -320.473 & 980.151 \\ 315.9 & -353.737 & 952.154 \\ 337.7 & -355.198 & 924.931 \\ 337.6 & -417.371 & 919.138 \\ 338.7 & -463.376 & 911.577 \\ 343.7 & -480.500 & 899.291 \\ 173.7 & -315.709 & 956.824 \\ 288.2 & -310.258 & 938.918 \\ 326.7 & -361.738 & 889.594 \\ 303.6 & -360.580 & 903.375 \\ 278.5 & -362.122 & 918.553 \\ 325.5 & -386.234 & 861.597 \\ 328.4 & -453.600 & 848.690 \\ 149.7 & -281.362 & 951.828 \\ \end{array}$	(298)(g. 298)(298) $\Delta_{sub}H^{\circ}(0)$ 175.1 -326.632 999.236176.468235.5 -320.473 980.151236.964315.9 -353.737 952.154317.269337.7 -355.198 924.931339.045337.6 -417.371 919.138338.920338.7 -463.376 911.577339.944343.7 -480.500 899.291344.936173.7 -315.709 956.824175.226288.2 -310.258 938.918290.047326.7 -361.738 889.594328.921303.6 -360.580 903.375305.774278.5 -362.122 918.553280.633325.5 -386.234 861.597327.594328.4 -453.600 848.690330.475149.7 -281.362 951.828151.700	(298)(g, 298)(298) $\Delta_{sub}H^{\circ}(0)$ $\Delta_{f}H^{\circ}(g, 0)$ 175.1 -326.632 999.236176.468 -325.432 235.5 -320.473 980.151236.964 -317.843 315.9 -353.737 952.154317.269 -352.700 337.7 -355.198 924.931339.045 -354.083 337.6 -417.371 919.138338.920 -415.873 338.7 -463.376 911.577339.944 -463.017 343.7 -480.500 899.291344.936 -477.699 173.7 -315.709 956.824175.226 -313.054 288.2 -310.258 938.918290.047 -306.450 326.7 -361.738 889.594328.921 -358.765 303.6 -360.580 903.375305.774 -358.606 278.5 -362.122 918.553280.633 -360.944 325.5 -386.234 861.597327.594 -384.687 328.4 -453.600 848.690330.475 -452.014 149.7 -281.362 951.828151.700 -280.172

TABLE 62 Recommended enthalpies of sublimation, formation, and atomization (k/mol) for lanthanide dichlorides^{*a*}

^a The error in the enthalpies is estimated to be ±3 kJ/mol. All primary (experimental) enthalpy values are given with an accuracy of 0.1 kJ/mol. Other values calculated from them have an accuracy of 0.001 kJ/mol, as accepted in IVTANTERMO (2004).

et al., 1984) for GdCl₂ only. Conversely, the results of $AE(R^+/RCl_2)$ measurements (Hariharan et al., 1972; Sapegin, 1984; Sapegin et al., 1984) were ignored in selecting the recommended values for NdCl₂, SmCl₂, EuCl₂, DyCl₂, TmCl₂, and YbCl₂. For all the other compounds, experimental values obtained by the two specified methods were averaged.

Several $\Delta_{sub}H^{\circ}(298)$ values were calculated only using the results of $K_{p}^{\circ}(T)$ measurements for the corresponding gas-phase reactions. These are the values recommended for LaCl₂, NdCl₂, DyCl₂, HoCl₂, ErCl₂, TmCl₂, and LuCl₂. For three compounds (NdCl₂, DyCl₂, and TmCl₂), equilibrium constants were measured for reactions of the corresponding lanthanide with BaCl₂ and EuCl₂. The $\Delta_{sub}H^{\circ}(298)$ values recommended for NdCl₂ and DyCl₂ were obtained by averaging the data on these two reactions. The $\Delta_{sub}H^{\circ}(298)$ value recommended for TmCl₂ was obtained by $K_{p}^{\circ}(T)$ measurements for the reaction of Tm with EuCl₂; this value better fits into the dependence of $\Delta_{sub}H^{\circ}(298)$ on the atomic number of R. Table 62 also contains the recommended enthalpies of atomization of RCl₂ calculated after the determination of the series of $\Delta_{sub}H^{\circ}(298)$ values. The $\Delta_{at}H^{\circ}$ (PmCl₂, 298) enthalpy was calculated from the $\Delta_{sub}H^{\circ}(PmCl_2, 298)$ value estimated according to the dependence of RCl₂ compounds.

The logP (Pa) = 10.037 - 13,780/T (T = 1000-1400 K) semilogarithmic plot was suggested by Kudin et al. (1993b) to describe the temperature dependence of saturated vapor pressure over NdCl₂. This dependence contains two errors. First, the temperature range specified should include both sublimation and vaporization temperatures of neodymium dichloride; it follows that there should be two different graphs for this temperature range. Next, with the coefficients specified, the calculated pressure values can only be realistic if the left-hand side contains the natural rather than decimal logarithm of vapor pressure. Close to the estimated melting point (1098 K), we would then have $\Delta_{sub}H^{\circ}$ (298, III law) = 337.3 kJ/mol and $\Delta_{sub}H^{\circ}(298, II law) = 286.7 kJ/mol$ (if the semilogarithmic plot describes sublimation) or 325.7 kJ/mol (if the graph describes vaporization). If our suggestions of the source of errors in Kudin et al. (1993b) are correct, the thermodynamic functions of NdCl₂ give the enthalpy of sublimation (third law) that coincides with the equilibrium constant data (see Table 61) to within ~ 1 kJ/mol.

9.4 Recommended data for lanthanide dichlorides

The enthalpies of sublimation, formation, and atomization recommended by us are summarized in Table 62 for the standard temperature 298.15 K. The data obtained allowed us to calculate these characteristics for standard temperature 0 K (see Table 62) using the needed parameters from
IVTANTERMO (2004) and the enthalpies of formation of crystalline lanthanide dichlorides from Table 55.

10. THERMODYNAMIC FUNCTIONS FOR LANTHANIDE MONOHALIDE MOLECULES

10.1 Thermodynamic functions for LaF and LaCl molecules

The thermochemical properties of gaseous lanthanide halides have been extensively studied over several decades. However, the available data are insufficient for adequate thermodynamic modeling of the high-temperature processes involving monohalides. For RX (R = La–Lu; X = F, Cl, Br, I), no information was available on the thermodynamic functions until recently. This gap was partially filled by the data reported by Chervonnyi and Chervonnaya (2004d), who calculated the thermodynamic functions of RCl in the ideal gas state in the temperature range 298.15–3000 K at the standard pressure. These data were also used for determining $\Delta_{at}H^{\circ}$ (RX, 0) from the experimental equilibrium constants K_p° of gas-phase reactions for some monochlorides such as LaCl (Chervonnyi and Chervonnaya, 2004b), SmCl (Chervonnyi and Chervonnaya, 2004e), EuCl (Chervonnyi and Chervonnaya, 2004b), and YbCl (Chervonnyi and Chervonnaya, 2004f).

Two factors prevent this problem from being completely solved. First, no experimental data are available dealing with the equilibria involving other lanthanide monohalides, except monofluorides, which have been comprehensively addressed. Indeed, equilibrium constants for 30 gas-phase reactions involving RF_k (R = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm; k = 1–3) were measured by mass spectrometry (Hildenbrand and Lau, 1995; Kleinschmidt et al., 1981; Zmbov and Margrave, 1966a,c, 1967a, 1968). From these data, $\Delta_{at}H^{\circ}(RX, 0)$ values for nine of the fifteen monofluorides RF can be calculated.

Second, the choice of the appropriate approximation for calculating thermodynamic functions by statistical thermodynamic methods presents some difficulties. If we restrict our consideration to monofluorides and monochlorides and survey the literature data required for the calculation of thermodynamic functions, the following picture is revealed. Based on experimental data (Azuma et al., 1991; Barrow and Chojnicki, 1975; Barrow et al., 1967; Bernard et al., 2000a,b, 2001, 2002; Bloch et al., 1996; Clements and Barrow, 1984; Cooke et al., 2005; Dick and Linton, 2001, 2004, Dick et al., 2005; Dickinson et al., 2001; Dunfield et al., 1995; Effantin et al., 1976, 2002; Gatterer et al., 1942; Gurvich et al., 1989; Kaledin et al., 1992, 1994a,b, 1996b, 1997, 1998; Kramer, 1978a,b; Lee and Zare, 1977; Linton and Adam, 2001; Linton et al., 2005; Lumley and Barrow, 1978;

McCarthy et al., 1996; Melville et al., 2000; Robbins and Barrow, 1974; Rubinoff et al., 2003; Sauer et al., 1996; Schall et al., 1983, 1987; Shenyavskaya et al., 1965, 1968; Simard and James, 1992; Uttam and Joshi, 1995; Uttam et al., 1997; Vergès et al., 1999; Xin and Klynning, 1994), molecular constants for most fluorides RF and some chlorides RCl have been determined only for the ground electronic state. These data are sufficient for reasonably estimating molecular constants for unknown compounds in this state. Thus, the possibility appears to use the rigid rotator–harmonic oscillator model in calculations of the thermodynamic functions for the entire series of RF and RCl molecules.

It should be taken into account that lanthanide compounds have a large number of excited electronic states. Although molecular constants for these states are unknown, their contribution to the thermodynamic functions can be considered by introducing a calculated correction (Gurvich et al., 1978–1984) to the electronic ground-state component. For lanthanide halides as ionic compounds, the correction can be calculated using the electronic excitation energies of the free R⁺ ions.

For RX, there is an alternative method for calculating this correction. Kaledin et al. (1996a) described the molecular electronic states of RX (R = Ce-Yb and X = F, Cl, Br, I) in a wide range of energies in terms of the ligand field theory (LFT), which takes into account the perturbation of the energy levels of the R^+ ion by the ligand X^- . These results were supported by DFT calculations of low-lying electronic states for RF (Dai et al., 1998; Ren et al., 1998).

Considerable differences in excitation energies and statistical weights for similar RX and R⁺ species (see Dai et al., 1998; Kaledin et al., 1996a; Martin et al., 1978; Ren et al., 1998) lead to noticeable differences in their thermodynamic functions. This fact was a stimulus for this work (Chervonnyi and Chervonnaya, 2007d,e). We believe that the applicability of one of the two methods of inclusion of the electronic contribution will be demonstrated by thermodynamic analysis of the corresponding experimental data. For this purpose, we selected measured K_p° values by several authors (Chervonnyi and Chervonnaya, 2004a,b,e,f, 2005b; Hildenbrand and Lau, 1995; Kleinschmidt et al., 1981; Zmbov and Margrave, 1966a,c, 1967a, 1968).

The solution of this problem entailed the study of seemingly specific problems: we calculated the thermodynamic functions of gaseous lanthanide difluorides (Chervonnyi and Chervonnaya, 2007c) and determined the IEs of the RF and RCl molecules (Chervonnyi and Chervonnaya, 2007f). It is worth noting that these parameters are essential for the thermodynamic modeling of high-temperature processes. In particular, $\Delta_{at}H^{\circ}(RX^{+}, 0)$ can be calculated from the IE(RX) and $\Delta_{at}H^{\circ}(RX, 0)$ values. Knowledge of these functions is necessary, for example, when studying processes with the participation of lanthanide halides in the

low-temperature plasma state, in which, even at 5000–6000 K, the concentration of molecular ions is comparable with or higher than the concentration of the molecules (Kaledin et al., 1998).

The most reliable method of determining the thermodynamic functions involves representing a molecule as a nonrigid rotator and an anharmonic oscillator and calculating statistical sums by direct summation over energy levels. Such a procedure is for the moment possible only for LaF and LaCl. The experimental and theoretical data on the structures and spectra (Xin and Klynning, 1994; Kaledin et al., 1997; Vergès et al., 1999; Bernard et al., 2000a,b, 2001, 2002; Fahs et al., 2002, 2004; Chen and Shang, 2003a,b; Rubinoff et al., 2003; Cao and Dolg, 2005) of these molecules make it possible to presumably consider all electronic excited states that make noticeable contributions to the thermodynamic functions (T = 298.15 - 3000 K) when the latter are calculated with a high degree of precision. However, this is not the only aim of the present work. Parallel calculation of the thermodynamic functions for LaX in the rigid rotatorharmonic oscillator approximation, with appropriate corrections for electronic excitation, allows us to estimate not only the error of this model in the reduced Gibbs energy magnitude but also the effect of this factor on $\Delta_{at}H^{\circ}(RX, 0)$. The totality of these data is required to assess the degree of confidence in the analogous data reported by us for the entire series of RF and RCl.

10.1.1 Molecular constants

The molecular constants of LaF and LaCl in the states with excitation energies far beyond 10,000 cm⁻¹ are known (Xin and Klynning, 1994; Kaledin et al., 1997; Vergès et al., 1999; Bernard et al., 2000a,b, 2001; Bernard et al., 2002; Fahs et al., 2002, 2004; Chen and Shang, 2003a,b; Rubinoff et al., 2003; Cao and Dolg, 2005). Here, we restrict our consideration only to those that have excitation energies in the range 0–10,000 cm⁻¹. This range is sufficient to calculate the thermodynamic functions in the range 298.15–3000 K without losing accuracy due to the exclusion of other states.

The rotational structure of the absorption bands in the visible range was measured, and the interatomic distance R_e ($R_e = 2.026$ Å) and rotational constant B_e ($B_e = 0.2458$ cm⁻¹) were determined for LaF in the ground electronic state (Barrow et al., 1967). These authors acknowledged that the fundamental vibrational frequency $\Delta G_{1/2}$ (682 and 657 cm⁻¹) was overestimated and recommended $\Delta G_{1/2} = 550$ cm⁻¹. Schall et al. (1983), in the course of the observation of transitions to the X¹Σ⁺ and (1)³Δ states in the laser-induced fluorescence spectra of LaF, detected the electronic excited states (1)³Δ₁, (1)³Δ₂, and presumably (2)¹Δ. Their energies T_e are 1432, 1808, and 5478 cm⁻¹, respectively. The original molecular constants (Barrow et al., 1967; Schall et al., 1983) were used by Hildenbrand and Lau (1995) for calculating the thermodynamic functions of LaF, although the authors referred to the known handbook (Huber and Herzberg, 1979) as the source of the values of the vibrational constant ω_e (570 cm⁻¹), the anharmonicity constant $\omega_e x_e$ (2.3 cm⁻¹), and B_e (0.2456 cm⁻¹) for the ground electronic state of this molecule. The fact is that the values reported in this handbook (Huber and Herzberg, 1979) are corrected but unpublished data by Barrow et al. (1970).

Based on the spectroscopic studies (Kaledin et al., 1994b, 1997; Vergès et al., 1999; Bernard et al., 2000a,b, 2001, 2002), the molecular constants for the known electronic states of LaF were refined and their values for a number of new states were determined. The data reported in these works and the values of some molecular constants determined by us are summarized in Table 63.

Lanthanum monochloride LaCl has been less studied. Xin and Klynning (1994) reported molecular constants obtained from analysis of the rotational structure of IR bands in the thermal emission spectrum of LaCl recorded on a high-resolution Fourier transform spectrophotometer. It is worth noting that, despite a rather strong emission spectrum of LaCl, Xin and Klynning (1994) failed to detect the absorption spectrum of this compound. In this context, these authors selected, with low confidence and, apparently by analogy with the conclusions of Schall et al. (1983), the $^{1}\Sigma$ state, rather than the $^{3}\Delta$ state, as being the ground level. In addition, they did not determine the energy gap between these states. Based on observation of strong transitions to the Δ state, the conclusion was drawn that the excitation energy of the $(1)^{3}\Delta_{1,2,3}$ states is close to the ground-state energy. According to the estimate of Xin and Klynning (1994), this energy is ~ 1000 cm⁻¹. Similar values of some molecular constants of LaCl in the ground electronic state were later obtained by Rubinoff et al. (2003) from analysis of its rotational spectrum.

In addition to molecular constants for the ground state, values for some excited states were also reported (Xin and Klynning, 1994). These data are presented in Table 64. Comparison of the results from Tables 63 and 64 shows that both monohalides have the same sequence of states. This fact was emphasized by Xin and Klynning (1994) when they compared their findings with data for LaF from Schall et al. (1983).

In the framework of the present work, it is pertinent to mention the available *ab initio* calculations of the molecular properties of the compounds under consideration (Dolg and Stoll, 1989; Laerdahl, et al., 1998; Cao and Dolg, 2001, 2005; Hong et al., 2001; Cao et al., 2002; Fahs et al., 2002; Chen and Shang, 2003a,b; Fahs et al., 2004). Despite the lower accuracy of the calculated molecular constants (as compared to those determined spectroscopically), an advantage of *ab initio* calculations is that they reliably predict the electronic structure. The resulting data can be used either for interpreting the available experimental data or for

State	T _e	ω _e	$\omega_{\mathbf{e}} \mathbf{X}_{\mathbf{e}}$	$\omega_{ m e} y_{ m e} imes 10^3$	$\alpha_1 \times 10^3$	$\alpha_2 \times 10^6$	$eta_1 imes$ 10 ¹⁰	B _e	$D_{e} imes 10^{7}$	References
$X^1\Sigma^+$	0.0	575.205	2.125	-	1.246	-	-	0.246406	-	Kaledin et al. (1997)
$X^1 \Sigma^+$	0.0	575.20538	2.133415	2.1044	1.221682	-0.4398	4.6237	0.24637815	1.80968	Bernard et al. (2000a)
$X^1\Sigma^+$	0.0	574.948	2.11302	1.221594	-	-	_	-	_	Rubinoff et al. (2003)
$(1)^3\Delta_1$	1432	-	-	-	_	_	-	0.237786	1.828	Kaledin et al. (1994b)
$(1)^3\Delta_1$	1450.991	541.18947	2.02496	3.0280	1.208311	0.344	3.244	0.238400	1.8422	Bernard et al. (2000b)
$(1)^3\Delta_2$	1802.61	-	-	-	-	-	_	0.238263	1.836	Kaledin et al. (1994b)
$(1)^3\Delta_2$	1821.343	541.6920	2.03806	4.756	1.21598	4.628	6.42	0.2388891	1.8610	Bernard et al. (2000b)
$(1)^{3}\Delta_{3}$	2304.16	_	-	-	-	-	_	0.238647	1.840	Kaledin et al. (1994b)
$(1)^3\Delta_3$	2322.272	542.9279	2.025	3.0	1.23713	0.35	3.2	0.239314	1.869	Bernard et al. (2000b)
(2) ${}^{1}\Delta_{2}$	5494.011	-	-	-	-	-	_	0.237550	1.83	Kaledin et al. (1994b)
(2) $^{1}\Delta_{2}$	5494.011	542.9279	2.025	3.0	1.23713	0	3.2	0.237550	1.83	a
$(1)^{3}\Pi_{0}^{2}$	6593.42	509.32	-	-	-	-	-	0.22942	1.82	Vergès et al. (1999)

TABLE 63 Molecular constants of LaF (cm $^{-1}$)

$(1)^{3}\Pi_{1}$	6866.51	507.70	-	-	-	-	-	0.23013	1.88	Vergès et al. (1999)
$(1)^{3}\Pi_{2}$	7361.79	-	-	-	-	-	-	0.22999	1.91	Vergès et al. (1999)
(1) ³ Π	6964.7730	511.5978	1.94461	_	1.18784	-	2.75	0.23052044	1.86330	Bernard et al. (2001)
$(1)^{3}\Pi_{0}$	6593.420	511.5978	1.94461	0	1.18784	0	2.75	0.22942	1.82	а
$(1)^{3}\Pi_{1}$	6866.310	511.5978	1.94461	0	1.18784	0	2.75	0.23013	1.88	а
$(1)^{3}\Pi_{2}$	7361.790	511.5978	1.94461	0	1.18784	0	2.75	0.22999	1.91	а
$(1)^{1}\Pi$	8492.3720	501.19178	1.992379	3.5285	1.214460	0.5589	4.0907	0.22668432	1.85351	Bernard et al. (2000a)
$(1)^{3}\Phi_{2}$	10,927.192	474.04814	1.91733	3.761	1.22521	0.494	4.252	0.2235572	1.9833	Bernard et al. (2000b)
$(1)^{3}\Phi_{3}$	11,702.647	473.8508	1.9361	4.79	1.23069	0.17	1.710	0.2234926	1.9847	Bernard et al. (2000b)
$(1)^{3}\Phi_{4}$	12,205.359	-	-	-	-	-	-	0.225371	2.202	Bernard et al. (2000b)
$(1)^{3}\Phi_{4}$	12,505.359	473.8508	1.9361	4.79	1.23069	0	1.710	0.225371	2.202	a

^{*a*} Accepted in calculations by the direct summation method.

State	T _e	ω_{e}	$\omega_{\mathbf{e}}\mathbf{X}_{\mathbf{e}}$	$\omega_{\mathbf{e}}\mathbf{y}_{\mathbf{e}}$	$\alpha_1 \times 10^4$	$eta_1 imes$ 10 ¹¹	B _e	$D_{e} imes 10^{8}$	References
$\chi^1 \Sigma^+$	0.0	341.603	0.9797	0.00074	3.6399	6.9	0.096705	3.119	Xin and Klynning (1994)
$X^1\Sigma^+$	0.0	341.43	1.0014	-	3.64477	-	0.0967011	-	Rubinoff et al. (2003)
$(1)^3\Delta_1$	1010 ^a	321.7890	0.8819	0.0007 ^a	3.4956	1.5	0.093045	3.136	Xin and Klynning (1994)
$(1)^3\Delta_2$	1267 ^a	322.082	0.8797	0.0007 ^a	3.4852	4.2	0.093145	3.135	Xin and Klynning (1994)
$(1)^3\Delta_3$	1616 ^a	323.053	0.8833	0.0007 ^a	3.491	2.6	0.093309	3.165	Xin and Klynning (1994)
$(2)^1\Delta_2$	3823	323.2	0.8876	0	3.315	6.24	0.09212	2.994	a
$(1)^{3}\Pi_{0}$	4588	305.4	0.8282	0	3.180	5.82	0.08875	2.998	а
$(1)^{3}\Pi_{1}$	4778	305.4	0.8282	0	3.193	5.84	0.08904	3.027	а
$(1)^{3}\Pi_{2}$	5123	305.4	0.8282	0	3.190	5.85	0.08899	3.022	а
(1) ¹ Π	5957.838	301.0150	0.8603	0	3.5584	5.7	0.089284	3.112	Xin and Klynning (1994)

TABLE 64Molecular constants of LaCl (cm $^{-1}$)

$(1)^{3}\Phi_{2}$	7067.255	284.4862	0.7795	0.0113 ^a	3.4019	6.0	0.086743	3.226	Xin and Klynning (1994)
$(1)^{3}\Phi_{3}$	7425.701	283.474	0.8426	0.0113 ^a	3.4985	5.3	0.086704	3.278	Xin and Klynning (1994)
$(1)^{3}\Phi_{4}$	7583.046	283.524	0.8488	0.0113 ^a	3.456	9.6	0.086839	3.27	Xin and Klynning (1994)
$(1)^1\Sigma^+$	9556.807	291.570	0.278	-0.0185	3.79	4.96	0.088811	3.245	Xin and Klynning (1994)

^{*a*} Accepted in calculations by the direct summation method.

assessing molecular constants when experimental data are lacking. Keeping in mind the results of the above-mentioned studies, we would like to focus on four aspects that are of direct significance for the problems under consideration: (i) analysis of the accuracy of the calculation of R_e and ω_e for the ground state, (ii) the values of the enthalpies of atomization, (iii) the trends in the change in molecular constants for excited states, and (iv) the attempt to determine the ground-state term from the energy of the molecule.

In our opinion, comparison of the achieved accuracy of the values of molecular constants R_e and ω_e , which were in most cases calculated for the ground state, makes it possible to formulate a definite degree of confidence for the numerical values of enthalpies of atomization (Chen and Shang, 2003a,b; Cao and Dolg, 2005), as well as for the T_e values for excited states (Fahs et al., 2002, 2004). It is also of interest to compare the calculated total energies of the molecules, which are used for assigning the symmetry of the ground state (Chen and Shang, 2003a,b).

The molecular constants for LaF, obtained by theoretical calculations, are as follows (in order of publication): $R_e = 2.038$ Å, $\omega_e = 571$ cm⁻¹ (Laerdahl, et al., 1998); $R_e = 2.034$ Å, $\omega_e = 574$ cm⁻¹ (Cao and Dolg, 2001); $R_e = 2.031$ Å, $\omega_e = 570$ cm⁻¹ and $R_e = 2.033$ Å, $\omega_e = 568$ cm⁻¹ (Hong et al., 2001); $R_e = 2.027$ Å, $\omega_e = 578$ cm⁻¹ and $R_e = 2.034$ Å, $\omega_e = 574$ cm⁻¹ (Cao et al., 2002); $R_e = 2.057$ Å, $\omega_e = 583.4$ cm⁻¹ (Fahs et al., 2002); $B_e = 0.24299$ cm⁻¹, $\omega_e = 575.3$ cm⁻¹ and $B_e = 0.24390$ cm⁻¹, $\omega_e = 573.6$ cm⁻¹ (Cao and Dolg, 2005). In Chen and Shang (2003a), the rotational constants are reported. As follows from the calculation, for $B_e = 0.24299$ and 0.24390 cm⁻¹, R_e is equal to 2.038 and 2.034 Å, respectively. Thus, the R_e values are within the range 2.027–2.057 Å and the ω_e values are within the range 568–583.4 cm⁻¹. Their difference from the corresponding experimental data is no more than ~1.5%.

As for the analogous data for LaCl, the results of three independent calculations are available: $R_e = 2.514$ Å and $\omega_e = 343$ cm⁻¹ (Chen and Shang, 2003b), $R_e = 2.578$ Å and $\omega_e = 331$ cm⁻¹ (Fahs et al., 2004), and $R_e = 2.517$ Å and $\omega_e = 339$ cm⁻¹ (Cao and Dolg, 2005). Comparison of these values with the experimental data (Xin and Klynning, 1994) shows that, in two cases, the difference is even smaller (~1%). The exception is the values calculated by Fahs et al. (2004), which deviate from the experimental ones by ~4%.

The aforementioned identical sequence of excited states for the LaF and LaCl molecules is also supported by theoretical calculations (Fahs et al., 2002, 2004). These are the first data on excited states found by *ab initio* methods. The T_{e} , R_{e} , and ω_{e} values were calculated for all experimentally observed states and estimated for new triplet transitions,

including the excited state $(2)^{3}\Pi$, as well as for the experimentally unobserved $(1)^{3}\Sigma^{+}$ state (Fahs et al., 2002, 2004).

Comparison of our calculated data with the corresponding experimental results shows that the average deviations for LaF are $\Delta T_e = 95 \text{ cm}^{-1}$, $\Delta R_e = 0.033 \text{ Å}$, and $\Delta \omega_e = 5 \text{ cm}^{-1}$. For LaCl, an analogous comparison with the data reported by Xin and Klynning (1994) reveals somewhat larger differences. In particular, ΔT_e is 110 cm⁻¹ for low-lying states and can be as large as 978 cm⁻¹ for high-lying states. The ΔR_e values are within the range 0.08–0.09 Å, and the $\Delta \omega_e$ values fall within the range 3–17 cm⁻¹. As a rule, the theoretical values underestimate the experimental ones.

Assignment of the ground state to a definite type of symmetry is essential for calculating thermodynamic functions. Among the cited authors, only Chen and Shang (2003a,b) attempted to demonstrate whether the ground state has symmetry ${}^{1}\Sigma^{+}$ or ${}^{3}\Delta$. They optimized both states at the DFT/B3LYP level and decided in favor of the singlet state $X^{1}\Sigma^{+}$ as the ground state for LaF since this state had a lower total energy (by ~0.1 and ~0.15 eV for LaF and LaCl, respectively). This conclusion is consistent with the opinion of the authors of other experimental and theoretical studies.

10.1.2 Calculation of thermodynamic functions

The available set of the molecular constants for LaF and LaCl (Tables 63 and 64) allowed us to calculate the thermodynamic functions by three methods.

In the first method, the statistical sums over molecular states (including the electronic, vibrational, and rotational levels) were found by direct summation. Taking into account that the molecular constants reported by Vergès et al. (1999) and Bernard et al. (2000a,b, 2001) differ insignificantly (e.g., for the ground state) from the values published by Kaledin et al. (1997) and Rubinoff et al. (2003), and that this difference has little effect on the reduced Gibbs energy value, we used the molecular constants reported by the first authors in our calculations. The missing constants for the (2)¹ Δ_2 state in the report from Kaledin et al. (1994b) were taken to be the same as the analogous constants for the $(1)^3 \Delta_3$ state. The T_e values for the $(1)^{3}\Pi_{0}$, $(1)^{3}\Pi_{1}$, and $(1)^{3}\Pi_{2}$ states were taken from Vergès et al. (1999), and the other constants for these states were taken to be the same and they were taken from Kaledin et al. (1994b). Table 63 also contains data on the $(1)^3 \Phi_{2,3,4}$ states. The T_e values for them are above $10,000 \text{ cm}^{-1}$; therefore, their contribution to the thermodynamic functions is insignificant and can be ignored in the temperature range under consideration. Nevertheless, we present these data since they allow us to estimate the analogous quantities for LaCl, which has the $(1)^{3}\Phi_{2,3,4}$ states with T_e below 10,000 cm⁻¹. As follows from Table 63, some molecular constants for the $(1)^{3}\Phi_{3}$ and $((1)^{3}\Phi_{4}$ states of LaF are the same.

In the case of LaCl, in order to calculate the statistical sums over the molecular states by direct summation, we had to considerably extend the number of estimates of its molecular constants.

To do this, we determined how corresponding parameters change by examining the calculations by Fahs et al. (2002, 2004). It turned out that some ratios for the same state remain constant and do not depend on the type of symmetry of the state, that is, for the corresponding states, $T_e(\text{LaF})/T_e(\text{LaCl}) = 1.38 \pm 0.12$, $R_e(\text{LaCl})/R_e(\text{LaF}) = 1.25 \pm 0.01$, and $\omega_e(\text{LaF})/\omega_e(\text{LaCl}) = 1.80 \pm 0.08$. The constancy of these ratios was used for the selection of the missing T_e , R_e , and ω_e values for LaCl (Table 64). In addition, we assumed that similar constancy is also typical of the $\omega_e x_e(\text{LaF})/\omega_e x_e(\text{LaCl})$ ratio, which allowed us to estimate the missing data on the anharmonicity constant of LaCl in some states. In these estimates, we used selected data for LaF and the corresponding experimental values from Xin and Klynning (1994). Indeed, the known relationship

$$\omega_{\rm e} x_{\rm e} = \frac{\omega_{\rm e}^2}{4\Delta_{\rm at} H^{\circ}({\rm RX},0)},$$

where $\Delta_{at}H^{\circ}(RX, 0)$ is the enthalpy of atomization of LaX for estimating the anharmonicity constant results in too large errors for these compounds.

The other molecular constants were calculated using known relationships (Handbook, 1962; Gurvich et al., 1978–1984). From vibrational constants and the rotational constant, we found the centrifugal stretching constant D_e

$$D_{\rm e} = \frac{4B_{\rm e}^3}{\omega_{\rm e}^2},\tag{31}$$

the rovibrational constant α_1 ,

$$\alpha_1 = 6B_{\rm e}^2 \frac{\sqrt{\omega_{\rm e} x_{\rm e}/B_{\rm e}} - 1}{\omega_{\rm e}},$$
(32)

and the rovibrational constant β_1 ,

$$\beta_1 = D_e \left[8 \frac{\omega_e x_e}{\omega_e} - 5 \left(\frac{\alpha_1}{B_e} \right) - \frac{\omega_e}{24B_e} \left(\frac{\alpha_1}{B_e} \right)^2 \right].$$
(33)

The other constants ($\omega_e y_e$, $\omega_e z_e \alpha_2$, β_2) were unknown and taken to be zero in the equations for calculation of statistical sums.

In the second method, the thermodynamic functions were calculated in the rigid rotator–harmonic oscillator approximation with additional inclusion of the anharmonicity of oscillations by the method of Mayer and Goeppert-Mayer (Gurvich et al., 1978–1984) and correction for centrifugal stretching by relationships obtained for linear molecules (McDowell, 1963). The vibrational and rotational contributions were calculated from the molecular constants for the ground state of LaF (Bernard et al., 2000a) and LaCl (Xin and Klynning, 1994). The correction for electronic excitation was applied using the corresponding T_e values (Tables 63 and 64).

In the third method, the same approximation as in the second method was used for calculating the vibrational and rotational constants. The difference was that the contribution of electronic excitation was considered based on the electronic states observed for the free La⁺ ion. According to Martin et al. (1978), the energies (in cm⁻¹) of these states for La⁺ are as follows (the statistical weight of each state is given between parentheses): 0(5), 1016.10(7), 1970.70(9), 1394.46(5), 1895.15(3), 2591.60(5), 3250.35 (7), 5249.70(1), 5718.12(3), 6227.424(5), 7394.57(1), and 7473.32(9).

Figures 36 and 37 show the plots of the reduced Gibbs energy versus temperature. Curves *a* were plotted from the data obtained by Krasnov and Danilova (1969) by calculation of statistical sums only for the ground states of LaF and LaCl in the rigid rotator–harmonic oscillator approximation.

Above curve *a* in Figure 36, there are data points corresponding to the reduced Gibbs energies calculated from the data of Hildenbrand and Lau (1995), where the same approximation was used and, in addition, the



FIGURE 36 Reduced Gibbs energy vs. temperature for lanthanum monofluoride: data (*a*) from Krasnov and Danilova (1969), (*b*, *c*, *d*) calculated in this work, and (\blacktriangle) taken from Hildenbrand and Lau (1995). Reproduced from Chervonnyi and Chervonnaya (2007e) with permission from Pleiades Publishing, Ltd.



FIGURE 37 Reduced Gibbs energy versus temperature for lanthanum monochloride: data (*a*) from Krasnov and Danilova (1969), (*b*, *c*, *d*) calculated in this work. Reproduced from Chervonnyi and Chervonnaya (2007e) with permission from Pleiades Publishing, Ltd.

contributions from some electronic excited states of LaF were taken into account, again by using data from Hildenbrand and Lau (1995).

The above-lying and almost coincident curves *b* and *c* in Figures 36 and 37 represent the results of calculations of the reduced Gibbs energy by the method of Mayer and Goeppert-Mayer, with inclusion of electronic excitation according to the T_e values from Tables 63 and 64 (curves *b*) and by direct summation (curves *c*).

Curves *d* are the plots of the reduced Gibbs energy calculated by the method of Mayer and Goeppert-Mayer, but the contribution of electronic excitation was considered based on the electronic states observed for the free La^+ ion.

Both plots (Figures 36 and 37) clearly demonstrate the effect of electronic excitation on the reduced Gibbs energy. Indeed, in the temperature range in which the experimental data on K_p° of the reactions involving LaF ($T = \sim 2100$ K) and LaCl ($T = \sim 1400$ K) were processed, the increase in -[$G^{\circ}(T) - H^{\circ}(0)$]/*T* is ~16 J/(mol·K) in both cases.

Here, an important circumstance should be noted: the lower the T_e value, the higher the contribution due to each of the excited states. Comparison of the T_e values used in our calculations with the analogous data used by Hildenbrand and Lau (1995) does not account for the unreasonably large difference between the reduced Gibbs energies obtained by these authors (data points in Figure 36) and in our

calculations (curves *b* and *c*). As shown in Gurvich et al. (1978–1984), when the statistical sums are calculated, the statistical weights of all the states (${}^{3}\Delta$, ${}^{3}\Pi$, and ${}^{3}\Phi$ in this case), but not the Σ states, are doubled and, thereby, the additional splitting (so-called Λ doubling) of rotational levels is taken into account. Hildenbrand and Lau (1995) did not double the statistical weights which led to the significant discrepancies observed.

Comparison of the mutual arrangement of curves *b* and *c* in Figures 36 and 37 shows that the various methods used for calculating the statistical sums lead to close results at 298.15 K. The difference at this temperature is ~0.01 J/(mol·K) for LaF and ~0.03 J/(mol·K) for LaCl. With increasing temperature, these differences increase and become as large as ~1.22 (LaF) and ~0.86 (LaCl) J/(mol·K) at 3000 K. At temperatures of experimental data processing (T = ~2100 K for LaF and T = ~1400 K for LaCl), these differences are ~0.97 and ~0.60 J/(mol·K), respectively. Such a phenomenon is typical of calculations of statistical sums by direct summation over energy levels and in the rigid rotator–harmonic oscillator approximation (Handbook, 1962; Gurvich et al., 1978–1984).

The inclusion of the electronic contribution to the reduced Gibbs energy based on the electronic excitation energies of the free La⁺ ion leads to noticeable differences from the values calculated by the method of Mayer and Goeppert-Mayer. At 298.15 K, this difference is maximal (~13.4 J/(mol·K) for LaF and ~13.0 J/(mol·K) for LaCl). With increasing temperature, the difference decreases to ~6.4 (LaF) and ~3.4 (LaCl) J/(mol·K) at 3000 K. For moderate processing temperatures of experimentally measured K_p° values ($T = \sim 2100$ K for LaF and $T = \sim 1400$ K for LaCl), the differences in $-[G^\circ(T) - H^\circ(0)]/T$ (curves *b* and *d*) are equal to ~7.31 and ~4.85 J/(mol·K), respectively.

The reduced Gibbs energy obtained from the experimental data for LaCl (Xin and Klynning, 1994) differs by $\sim 0.2-0.4$ J/(mol·K) from the values based on the estimates of the molecular constants of this compound (Chervonnyi and Chervonnaya, 2004d).

The applicability of the resulting thermodynamic functions is further exemplified by the calculations of equilibria in gas-phase reactions involving LaF (Hildenbrand and Lau, 1995) and LaCl (Chervonnyi and Chervonnaya, 2004b) molecules. Available experimental values of K_p° for these reactions make it possible to trace changes in the enthalpies of reactions calculated by the third or second law ($\Delta_r H^{\circ}(0, \text{III law})$ and $\Delta_r H^{\circ}(0, \text{II law})$, respectively), as well as to compare the enthalpies of atomization derived from these values ($\Delta_{at}H^{\circ}(0, \text{III law})$ and $\Delta_{at}H^{\circ}$ (0, II law), respectively) depending on the thermodynamic functions used in the calculations. The results are summarized in Tables 65 and 66.

Tables 65 and 66 also present the temperature range in which $K_{\rm p}^{\circ}$ values were measured, its analytical dependence in the form $\log K_{\rm p}^{\circ} = A + B/T$, and the enthalpy of reaction $\Delta_{\rm r} H^{\circ}(T, \text{ II law})$ calculated

Parameter	$La + LaF_2 = 2LaF$	$\begin{array}{l} Ba + LaF_2 = \\ BaF + \ LaF \end{array}$	LaF + Ba = BaF + La
Reaction no.	(1)	(2)	(3)
T (K)	2008-2270	1917–2131	1984–2131
$T_{\rm Av}$ (K)	2140	2020	2060
A	0.101 ± 0.046	1.499 ± 0.055	1.002 ± 0.050
В	1167 ± 99	-3803 ± 113	-4276 ± 106
$\Delta_{\rm r} H^{\circ}(T, \operatorname{II law})$	-22.3 ± 1.9	72.8 ± 2.2	_
$\Delta_{\rm r} H^{\circ}(0, \text{III law})^{b}$	-17.1 ± 0.5	60.3 ± 0.4	80.0
$\Delta_{\rm r} H^{\circ}(0, \text{ II law})^{b}$	-23.1 ± 1.9	69.0 ± 2.2	_
$\Delta_{\rm r} H^{\circ}(0, \text{III law})^{c}$	-11.4 ± 0.5	50.2 ± 0.8	64.9
$\Delta_{\rm r} H^{\circ}(0, \text{ II law})^c$	-33.4 ± 1.9	67.8 ± 2.2	
$\Delta_{\rm r} H^{\circ}(0, {\rm III ~law})^d$	-15.7 ± 0.5	48.2 ± 0.8	66.9
$\Delta_{\rm r} H^{\circ}(0, \text{ II law})^d$	-30.1 ± 1.9	69.3 ± 2.2	_
$\Delta_{\rm r} H^{\circ}(0, \text{III law})^{e}$	15.5 ± 0.5	63.4 ± 0.5	51.7
$\Delta_{\rm r} H^{\circ}(0, \text{ II law})^{e}$	-18.7 ± 1.9	74.9 ± 2.2	_
$\Delta_{\rm at}H^{\circ}({\rm LaF, III law})^{b}$	657.4		660.0
$\Delta_{\rm at}H^{\circ}({\rm LaF}, 0, {\rm II \ law})^{b}$	672.1		_
$\Delta_{\rm at} H^{\circ}({\rm LaF}, 0, {\rm III \ law})^{c}$	641.6		644.9
$\Delta_{\rm at}H^{\circ}({\rm LaF}, 0, {\rm II \ law})^{c}$	681.2		
$\Delta_{\rm at} H^{\circ}({\rm LaF}, 0, {\rm III \ law})^d$	643.9		646.9
$\Delta_{\rm at} H^{\circ} ({\rm LaF}, 0, {\rm II \ law})^d$	679.4		_
$\Delta_{\rm at}H^{\circ}({\rm LaF}, 0, {\rm III \ law})^{e}$	627.9		631.7
$\Delta_{\rm at}H^{\circ}({\rm LaF}, 0, {\rm II \ law})^{e}$	673.6		_
$\Delta_{\rm at}H^{\circ}({\rm LaF}_2, 0, {\rm III \ law})^b$	1297.7		_
$\Delta_{\rm at}H^{\circ}({\rm LaF}_2, 0, {\rm II \ law})^b$	1321.1		_
$\Delta_{\rm at}H^{\circ}({\rm LaF}_2, 0, {\rm III \ law})^c$	1271.8		_
$\Delta_{\rm at}H^{\circ}({\rm LaF}_2, 0, {\rm II \ law})^c$	1329.0		_
$\Delta_{\rm at}H^{\circ}({\rm LaF}_2, 0, {\rm III \ law})^d$	1272.1		_
$\Delta_{\rm at}H^{\circ}({\rm LaF}_2, 0, {\rm II \ law})^d$	1328.7		_
$\Delta_{\rm at}H^{\circ}({\rm LaF_2}, 0, {\rm III \ law})^e$	1271.3		_
$\Delta_{\rm at}H^{\circ}({\rm LaF_2}, 0, {\rm II \ law})^e$	1328.5		_

TABLE 65 Equilibrium constants (log $K_{p}^{\circ} = A + B/T$), enthalpies (kJ/mol) of gas-phase reactions involving lanthanum fluorides, and enthalpies of atomization of LaF and LaF2 calculated using data from Hildenbrand and Lau (1995)^a

The thermodynamic functions of atomic barium and lanthanum, as well as of barium monofluoride were taken from IVTANTERMO (2004).

^b The data were obtained using the thermodynamic functions of LaF and LaF₂ calculated in the rigid rotatorharmonic oscillator approximation from the molecular constants reported by Hildenbrand and Lau (1995).

^c Data were obtained using the thermodynamic functions calculated by the direct summation method;

thermodynamic functions for $LaF_2(g)$ were taken from Chervonnyi and Chervonnaya (2007c).

^d Data were obtained using the thermodynamic functions calculated by the method of Mayer and Goeppert-Mayer with inclusion of the electronic excitation energies for LaF. The thermodynamic functions for $LaF_2(g)$ were taken from Chervonnyi and Chervonnaya (2007c).

^e Data were obtained using the thermodynamic functions calculated by the method of Mayer and Goeppert-Mayer with inclusion of the electronic excitation energies of the free La^+ ion. The thermodynamic functions of LaF₂(g) were taken from Chervonnyi and Chervonnaya (2007c).

by this equation and reduced to the average temperature (T_{Av}) of the temperature range. For convenience, each reaction is numbered. The errors for the determination of the coefficients *A* and *B* and for enthalpies are represented by root-mean-square deviations.

All reactions can be divided into two groups. The first one contains reactions in which the enthalpy of atomization of the compound under consideration is governed only by the enthalpy of reaction and the enthalpy of atomization of a reference compound determined in an independent study. These are reactions (3) (Table 65) and (4) (Table 66) involving BaF and BaCl, respectively. The enthalpies of atomization of these molecules, according to (IVTANTERMO, 2004), are as follows: $\Delta_{at}H^{\circ}(BaF, 0) = 580.0 \text{ kJ/mol and } \Delta_{at}H^{\circ}(BaCl, 0) = 440.0 \text{ kJ/mol.}$

It is worth noting that K_p° values for reaction (3) are not reported in Hildenbrand and Lau (1995), and that only its enthalpy $\Delta_r H^{\circ}$ (298) (79.9 ± 10.5 kJ/mol) is given. From this value, we calculated the K_p° values for the average measurement temperature (2058 K) using the thermodynamic functions reported by these authors. Then, from the resulting K_p° value, we determined the enthalpy of reaction (3) with the use of the thermodynamic functions selected in the current work (Table 65).

The second group includes reactions (1) and (2) (Table 65), involving lanthanum fluorides (Hildenbrand and Lau, 1995). Since there are two such reactions and, correspondingly, two sought enthalpies of atomization (for LaF and LaF₂) and since the $\Delta_{at}H^{\circ}(BaF, 0)$ value is known, the wanted quantities can be determined from the enthalpies of reactions (1) and (2), $\Delta_{r}H^{\circ}(1, 0)$ and $\Delta_{r}H^{\circ}(2, 0)$, respectively. We can then calculate the enthalpy of atomization of LaF₂ by the equation

$$\Delta_{at}H^{\circ}(LaF_{2},0) = 2[\Delta_{r}H^{\circ}(2,0) + \Delta_{at}H^{\circ}(BaF,0)] - \varDelta_{r}H^{\circ}(1,0)$$
(34)

and, then, the enthalpy of atomization of LaF using the relationship

$$\Delta_{\rm at} H^{\circ}({\rm LaF},0) = \frac{1}{2} [\Delta_{\rm at} H^{\circ}({\rm LaF}_2,0) - \Delta_{\rm r} H^{\circ}(1,0)]. \tag{35}$$

The thermodynamic functions for LaF₂ used for determining $\Delta_r H^{\circ}(1, 0)$ and $\Delta_r H^{\circ}(2, 0)$ have been described in Section 3. They were calculated in the rigid rotator–harmonic oscillator approximation with the inclusion of electronic excitation observed for the free La²⁺ ion.

As might be expected, the use of different thermodynamic functions for processing the experimental data (Hildenbrand and Lau, 1995; Chervonnyi and Chervonnaya, 2004b) led to different values of both the enthalpies of reactions and the enthalpies of atomization. The resulting difference is more pronounced for reactions (1)–(3).

The corrections applied to the thermodynamic functions involving a more complete inclusion of excited states and, more importantly,

Parameter	BaCl + La = Ba + LaCl
Reaction no.	(4)
T (K)	1380–1446
$T_{\rm Av}$	1413
Α	-0.417 ± 0.293
В	3375 ± 414
$\Delta_{\rm r} H^{\circ}(T, { m II law})$	-64.6 ± 7.9
$\Delta_{\rm r} H^{\circ}(0, { m III} { m law})^b$	-66.9 ± 0.5
$\Delta_{\rm r} H^{\circ}(0, \text{ II law})^b$	-69.0 ± 7.9
$\Delta_{\rm r} H^{\circ}(0, { m III} { m law})^c$	-60.1 ± 0.5
$\Delta_{\rm r} H^{\circ}(0, \text{ II law})^c$	-65.5 ± 7.9
$\Delta_{\rm at} H^{\circ}$ (LaCl, 0, III law) ^b	506.9 ± 0.5
$\Delta_{\rm at} H^{\circ}({\rm LaCl}, 0, {\rm II \ law})^{b}$	509.0 ± 7.9
$\Delta_{\rm at} H^{\circ}({\rm LaCl}, 0, {\rm III \ law})^{c}$	500.1 ± 0.5
$\Delta_{\rm at} H^{\circ}({ m LaCl},0,{ m II}\;{ m law})^c$	505.5 ± 7.9

TABLE 66 Equilibrium constants (log $K_{p}^{\circ} = A + B/T$) and enthalpies (in kJ/mol) of gasphase reactions involving lanthanum monochloride, calculated using data from Chervonnyi and Chervonnaya (2004b)^{*a*}

^{*a*} Thermodynamic functions of atomic barium and lanthanum as well as of barium monochloride were taken from IVTANTERMO (2004).

^b Data were obtained using the thermodynamic functions calculated by the method of Mayer and Goeppert-Mayer with inclusion of the electronic excitation energies for LaCl. The use of the thermodynamic functions calculated by the direct summation method changes the enthalpy value by 0.5–0.8 kJ/mol.

^c Same calculation method but with inclusion of the electronic excitation energies of the free La⁺ ion.

including the doubling of the statistical weights for definite states, noticeably decrease the $\Delta_{at}H^{\circ}(\text{LaF}, 0, \text{III law})$ value. Despite the fact that this quantity was determined using the reactions involving LaF₂, it is in good agreement with the value obtained from measuring the K_{p}° value of reaction (3). This is due to the fact that corrections were simultaneously applied to the thermodynamic functions of lanthanum difluoride. The same factors are responsible for the decrease in the $\Delta_{at}H^{\circ}$ (LaF₂, 0, III law) value.

Inasmuch as the values of the enthalpy of atomization of lanthanum monofluoride measured by other experimental methods are not available, the values obtained in this work can only be compared to the results of theoretical calculations. In particular, Chen and Shang (2003a) calculated $\Delta_{at}H^{\circ}$ (LaF, 0) by various methods and obtained 649.0 (B3LYP), 642.5 (CCSD(T)), and 680.9 (MP2) kJ/mol. According to these authors, the first two values are more accurate than the last one. In addition, Cao and Dolg (2005) determined $\Delta_{at}H^{\circ}$ (LaF,0) = 649.4 kJ/mol by the relativistic effective core potential (RECP) method.

Despite the fact that the calculations of both enthalpies of atomization by the second law led to lower consistency than the above calculations, it should be considered that the thermodynamic functions used in their determination adequately describe high-temperature equilibria involving LaF and LaF₂. The use of the thermodynamic functions found with the inclusion of the electronic excitation energy of the free La⁺ ion leads to an error of about 10–15 kJ/mol for lanthanum monofluoride while this error is larger for lanthanum difluoride.

Analogous comparisons of the data for the reactions involving LaCl (Table 66) show a considerably smaller scatter of values. Going from the thermodynamic functions calculated with the inclusion, the electronic excitation energies of LaCl molecules, to the functions with the inclusion of the electronic excitation for the free La⁺ ion, leads to a decrease in $\Delta_{at}H^{\circ}$ (LaCl, 0, III law) by 5.8 kJ/mol. The resulting enthalpy of atomization is in better agreement with the value of 501.0 ± 7.7 kJ/mol determined by the electron-impact method (Sapegin, 1984). The enthalpies of atomization of LaCl obtained in *ab initio* calculations are even lower. In particular, Chen and Shang (2003b) reported the following values: 480.6 (B3LYP), 486.8 (QCISD(T)), and 654.9 (MP2) kJ/mol. The value closest to the experimental one (493.0 kJ/mol) was calculated by the RECP method (Cao and Dolg, 2005). The above tendencies are also observed when the data are processed by the second law.

In our opinion, the uncertainty in the symmetry of the ground state for LaF and LaCl still persists due to the lack of convincing evidence for one of the states. However, if we assume that the ground state of the LaF and LaCl molecules is the ${}^{3}\Delta$ state, the aforementioned difference in data (curves *b* and *d*) is leveled off. This leads, for example, to better agreement between of the enthalpies of atomization of LaCl determined by two independent methods (Sapegin, 1984; Chervonnyi and Chervonnaya, 2004b), as well as between these values and the corresponding theoretically calculated ones.

The above analysis shows that, in absence of adequate experimental and/or theoretical data on the molecular constants of lanthanum mono-fluorides and monochlorides, their thermodynamic functions can be calculated by the method of Mayer and Goeppert-Mayer with inclusion of the electronic excited states observed for the free La⁺ ion.

10.2 Thermodynamic functions for RX (R = Ce-Lu) molecules

The results of our previous analysis (Chervonnyi and Chervonnaya, 2004d, 2007e) showed that, in the absence of sufficient experimental and/or theoretical data on the molecular constants of lanthanide mono-fluorides and monochlorides, their thermodynamic functions can be

calculated by the method of Mayer and Goeppert-Mayer with inclusion of excited electronic states observed for free R⁺ ions. However, due to the computation results (Kaledin et al., 1996a) obtained within the LFT approximation for the electronic excitation energies of RX (R = Ce–Yb; X = F, Cl), the electronic contribution can also be taken into account based on these data. This section deals with the calculation of the reduced Gibbs energy of the compounds under consideration in the ideal gas state in the temperature range 298.15–3000 K at standard pressure and based on the available molecular constants of RF (R = Ce–Lu) for the ground state with the inclusion of corrections for electronic excitation by two methods.

10.2.1 Molecular constants for RF molecules

The lanthanide compounds under consideration have a large number of excited electronic states (Kaledin et al., 1996a), which complicates the interpretation of spectroscopic data. In particular, the molecular constants for the ground state cannot be always determined. The available data should be preliminarily tested for reliability, and missing data should be completed. To this end, a semiempirical approach is possible in which the results are checked for correspondence with the known principle of the change in a given parameter in a series of related compounds.

We have previously showed that the dependence of the molecular constants of RCl₂, RCl₃, and RF₃ on the atomic numbers of the R atom in the 4f series among similar compounds is described with a high degree of accuracy by polynomial (1) given in Section 2.

The use of polynomial (1) for estimating the molecular constants of these compounds and the calculation of the thermodynamic functions from these molecular parameters lead to reliable results. This has been demonstrated by calculations of different equilibria involving gaseous RF₃, RCl₃, and RCl₂.

The effect of lanthanide contraction for monofluorides has been considered by Wang and Schwarz (1995). DFT calculations in this work showed that in going from LaF to LuF, the interatomic distance decreases by 0.12 Å. Küchle et al. (1997) subsequently demonstrated that the influence of interatomic distances on the other molecular constants (R_{e} , ω_{e}) of lanthanum and lutetium monofluorides is reflected by calculations with the pseudopotential method.

Calculations of the rovibrational component of statistical sums in the rigid rotator–harmonic oscillator approximation with inclusion of additional corrections for the anharmonicity of oscillations require data on a number of molecular constants: ω_e , $\omega_e x_e$, α_1 , D_e , and B_e (or R_e) (Handbook, 1962; Gurvich et al., 1978–1984).

As follows from the analysis of spectroscopic data (Azuma et al., 1991; Barrow and Chojnicki, 1975; Barrow et al., 1967; Bernard et al., 2000a,b, 2001, 2002; Bloch et al., 1996; Clements and Barrow, 1984; Cooke et al., 2005; Dick et al., 2005; Dickinson et al., 2001; Dunfield et al., 1995; Effantin et al., 1976, 2002; Gurvich et al., 1989; Kaledin et al., 1992, 1994a,b, 1996b, 1997, 1998; Lee and Zare, 1977; Lumley and Barrow, 1978; McCarthy et al., 1996; Robbins and Barrow, 1974; Rubinoff et al., 2003; Sauer et al., 1996; Schall et al., 1983, 1987; Shenyavskaya et al., 1965, 1968; Simard and James, 1992; Uttam and Joshi, 1995; Vergès et al., 1999), these constants have been determined for 10 of the 15 RF compounds (LaF, CeF, EuF, GdF, TbF, DyF, HoF, TmF, YbF, and LuF). The monofluorides PrF, NdF, PmF, SmF, and ErF have not heretofore been studied. Table 67 summarizes the results reported in these works with reference to the ground state of RF. Their correspondence to Eq. (1) was estimated by the least-squares method. The corresponding unknown constant was calculated based on the polynomial obtained for each of the molecular constants.

Indeed, polynomial (1) can describe, with a high degree of accuracy, almost all available experimental values of R_e and ω_e as a function of n (see Figures 38 and 39). Only the constants for three monofluorides—CeF, EuF, and YbF—are exceptions. For CeF, there is a noticeable deviation from the smooth curve, and for the other two compounds, this deviation is anomalous. Because of a lack of confidence in the molecular constants for the ground state of CeF (Azuma et al., 1991; Bloch et al., 1996; Clements and Barrow, 1984), these parameters were excluded from processing along with the data for EuF and YbF.

For comparison, Table 67 presents, in addition to the experimental data, the values calculated from approximating polynomials. As can be seen, the mutual deviations of the vibrational constant in most cases do not exceed 2 cm⁻¹ (for CeF, this deviation is ~8 and ~28 cm⁻¹ with respect to the two sets of experimental data). Analogous differences in interatomic distances between calculated and experimental data are in most cases not higher than 0.015 Å (for CeF, this difference is ~0.034 Å). These comparisons were performed not only for justifying the exclusion of the data on CeF from the calculations but also for clearly estimating the error of approximation.

Similar comparisons reveal the anomalous character of the molecular constants of EuF and YbF: they deviate from the common series of values by $\sim 110 \text{ cm}^{-1}$ for the vibrational constant and by $\sim 0.09-0.11$ Å for the interatomic distance. This also follows from the experimental study of the molecular constants of YbCl (Dickinson et al., 2001; Gatterer et al., 1942; Kramer, 1978b; Lee and Zare, 1977; Linton and Adam, 2001; Melville et al., 2000; Uttam and Joshi, 1995) in comparison with analogous data for LuCl

R	⊿G _{1/2}	ω _e	$\omega_{\mathbf{e}}\mathbf{X}_{\mathbf{e}}$	B _e	R _e (R—F)	$\alpha_1 imes 10^3$	$D_{e} imes 10^{7}$	References
La	-	682/657 (550)	-	-	2.026	-	-	Barrow et al. (1967)
		570		0.24562	2.0263		1.78	Barrow et al. (1970)
	-	-	_	0.245786	-	_	1.88	Simard and James (1992)
	_	575.205	2.125	0.246406	2.0233	1.246	1.834	Kaledin et al. (1997)
	_	575.20538	2.133415	0.24637815	2.0234	1.221682	1.80968	Bernard et al. $(2000a)^b$
	_	574.948	2.11302	0.24637656	2.02335060	1.22166	1.81199	Rubinoff et al. (2003)
Ce	_	589	_	0.240182	2.0484	-	-	Clements and Barrow (1984)
	-	_	_	0.240322	_	1.2	1.811	Azuma et al. (1991)
	549.2	553.3	2.05	_	2.048	_	_	Bloch et al. (1996)
	576.9	581.2	2.17	0.24827	2.014	1.24	1.81	Ь
Pr	582.5	586.9	2.21	0.25046	2.005	1.26	1.82	b
Nd	587.6	592.1	2.25	0.25207	1.996	1.28	1.83	b
Pm	592.1	596.7	2.28	0.25415	1.987	1.30	1.84	b
Sm	596.2	600.8	2.32	0.25527	1.978	1.31	1.84	b
Eu	_	493.06	_	0.2300	_	1.42	1.3	Gurvich et al. (1989)
	489.3	493.06	1.90	0.23000	2.083	1.21	2.00	b
Gd	_	606.8	2.3	0.25858	_	1.56	1.89	Kaledin et al. (1996b)
	602.8	607.6	2.38	0.25818	1.963	1.34	1.86	b
Tb	611.16	_	_	_	1.9596	_	-	Lumley and Barrow (1978)
	611.18	_	-	_	_	_	_	Kaledin et al. (1994a)
	605.4	610.2	2.40	0.25986	1.955	1.36	1.88	b

TABLE 67 Fundamental vibrational frequency $\Delta G_{1/2}$ and other molecular constants for the ground state of RF^{*a*}

Dy	$\sim\!605$	-	_	0.261	_	_	1.8	McCarthy et al. (1996)
-	-	610	2.22	0.262	1.945	1.16	1.93	Kaledin et al. (1998)
	607.4	612.3	2.42	0.26116	1.948	1.37	1.90	b
Но	-	615.28	2.603	0.26295	1.9399	1.45	1.78	Robbins and Barrow (1974)
	_	615.214	2.60	0.262380	_	_	1.967	Kaledin et al. (1992)
	-	615	2.30	0.263	1.940	1.18	1.92	Kaledin et al. (1998)
	609.0	613.9	2.44	0.26259	1.941	1.38	1.92	b
Er	610.1	615.0	2.45	0.26397	1.935	1.39	1.94	b
Tm	-	615	2.39	0.265	1.930	1.23	1.97	Kaledin et al. (1998)
	610.6	615.5	2.45	0.26539	1.928	1.40	1.97	b
Yb	-	506.32	2.205	0.24140	2.016	-	2.162	Barrow and Chojnicki (1975)
	_	506.6674	2.2451	0.242191	_	1.550	2.3888	Dunfield et al. (1995)
	_	505.5	1.9	_	_	_	_	Uttam and Joshi (1995)
	-	_	_	0.2412927	_	_	_	Sauer et al. (1996)
	-	_	_	0.24204405	2.016514	1.49894	_	Dickinson et al. (2001)
	501.7	505.5	1.90	0.24219	2.016	1.25	2.22	b
Lu	-	611.79	2.54	0.26764	1.9171	1.56	2.04	Effantin et al. (1976)
	-	618	2.82	_	1.91711815	1.562	2.011	Cooke et al. (2005)
	610.2	615.1	2.45	0.26758	1.917	1.41	2.02	b

^{*a*} All molecular constants are in cm⁻¹, except for the interatomic distance expressed in Å. ^{*b*} From polynomial approximation; accepted in calculations of the thermodynamic functions.



FIGURE 38 The interatomic distance in RF molecules. ▲, Taken from the experimental data (see Table 67). Accepted values used in calculations are shown by the solid line.



FIGURE 39 Vibrational constant ω_e in RF molecules. \blacktriangle , Taken from the experimental data (see Table 67). Accepted values used in calculations are shown by the solid line.

(Cooke et al., 2005; Kramer, 1978a). In addition, the ω_e and R_e values for many monofluorides have been calculated with satisfactory accuracy by *ab initio* pseudopotential and DFT methods (Cao et al., 2002; Chen and Shang, 2003a; Dolg and Stoll, 1989, 1996; Dolg et al., 1991, 2000; Heiberg et al., 2003; Hong et al., 2001; Küchle et al., 1997; Liu et al., 1998). In some cases, the difference from the experimental ω_e values is only a few cm⁻¹. For the interatomic distance, the difference is as large as several thousandths of an angstrom. Nevertheless, theoretical calculations also predict the anomalous behavior of the molecular constants of EuF and YbF.

Therefore, in calculations of thermodynamic functions, we used the ω_e and R_e values for EuF given by Gurvich et al. (1989). As for YbF, ω_e was taken from Uttam and Joshi (1995). The following reasons were behind this choice. The lack of data on the anharmonicity constant for some RF, on one hand, and, conversely, the presence of several noticeably different values for this constant for the same monofluoride, on the other hand, have forced us to search for an appropriate method for estimating this characteristic parameter. After examining some variants, we found that the dependence of $\omega_e x_e$ on ω_e has a smooth character. A similar relationship between ω_e and $\omega_e x_e$ is observed, for example, for alkaline-earth monofluorides and monochlorides (Gurvich et al., 1978–1984).

The relationship between $\omega_e x_e$ and ω_e was described by a secondorder polynomial based on 12 of the 15 available pairs of values for 8 monofluorides (Figure 40). The data for YbF (Barrow and Chojnicki, 1975; Dunfield et al., 1995) and LuF (Cooke et al., 2005) were not taken into account. This allowed us to subsequently calculate $\omega_e x_e$ for the entire RF series (see Table 67). Comparison of the calculated values with the corresponding experimental data shows that the discrepancy between them is no more than 0.16 cm⁻¹. Inasmuch as the data for YbF from Uttam and Joshi (1995) better fit the smooth curve reflecting the relationship between $\omega_e x_e$ and ω_e , these values were chosen for the calculations.

As it arises from Table 67, ω_e and $\omega_e x_e$ values have not been reported in some works, although they contain information on the fundamental vibrational frequency $\Delta G_{1/2}$. In order to include these results, the dependence of $\Delta G_{1/2}$ on *n* was checked based on all available data, including those for which no experimental results are available (Table 67) but can be calculated using the relationship

$$\Delta G_{1/2} = \omega_{\rm e} - 2\omega_{\rm e} x_{\rm e}.$$

These calculations were mainly performed to estimate the reliability of $\Delta G_{1/2}$ for TbF (Kaledin et al., 1996b; Lumley and Barrow, 1978) and DyF (McCarthy et al., 1996).



FIGURE 40 Anharmonicity constant vs. vibrational constant for RF molecules. (\blacktriangle) Taken from the experimental data (see Table 67). Accepted values used in calculation are shown by the solid line.

After choosing the ω_e , $\omega_e x_e$, and R_e values, D_e and α_1 were calculated by Eqs. (31) and (32). The resulting set of molecular constants used for calculating the translational and rovibrational components of the thermodynamic functions is shown in Table 67. The correction for centrifugal stretching was determined from the same data by the relationships obtained for linear molecules (McDowell, 1963).

10.2.2 Molecular constants for RCI molecules

Spectroscopic data on five lanthanide monochlorides have only been reported: LaCl (Xin and Klynning, 1994), DyCl (Linton et al., 2005), HoCl (Dick and Linton, 2001, 2004), YbCl (Dickinson et al., 2001; Gatterer et al., 1942; Lee and Zare, 1977; Linton and Adam, 2001; Melville et al., 2000; Uttam et al., 1997), and LuCl (Cooke et al., 2005; Kramer, 1978a).

Optical emission and absorption measurements gave some molecular constants for the ground and lower excited states of ytterbium monochloride. The emission spectrum (Gatterer et al., 1942) contains discrete bands in the wavelength range 4500–5800 Å. Analysis of this spectrum was only performed for the lowest four vibrational levels of each state. This allowed the observed spectral bands to be assigned to the $A^2\Pi_{1/2} - X^2\Sigma^+$ transition ($\omega_e = 293.1 \text{ cm}^{-1}$ and $\omega_e x_e = 1.34 \text{ cm}^{-1}$ for $X^2\Sigma^+$), $A^2\Pi_{3/2} - X^2\Sigma^+$ transition ($\omega_e = 294.1 \text{ cm}^{-1}$ and $\omega_e x_e = 1.12 \text{ cm}^{-1}$ for $X^2\Sigma^+$), and $B^2\Sigma^+ - X^2\Sigma^+$ transition ($\omega_e = 293.0 \text{ cm}^{-1}$ and $\omega_e x_e = 2.4 \text{ cm}^{-1}$ for $X^2\Sigma^+$). The T_e excitation energies into these states (17,892.4, 19,381.2, and 19,940.6 cm⁻¹) were obtained for the first time by Lee and Zare (1977) by analyzing the chemiluminescence spectrum of the YbCl molecule in the wavelength range 4500–5800 Å. The ground state $X^2\Sigma^+$ ($T_e = 0$) was characterized by the following constants: $\omega_e = 294.24 \text{ cm}^{-1}$ and $\omega_e x_e = 0.944 \text{ cm}^{-1}$; accordingly, $\Delta G_{1/2} = 290.35 \text{ cm}^{-1}$.

Closely similar energies for the $A^2\Pi - X^2\Sigma^+$ transitions (17,892.1 and 19,369.2 cm⁻¹) were obtained by Kramer (1978b), who studied the molecular emission of YbCl in a microwave discharge in the wavelength range 4600–6000 Å.

The emission spectrum of YbCl in the wavelength range 3800–6000 Å was reported by Uttam et al. (1997). The compound was vaporized from a graphite furnace, which allowed the authors to get rid of the masking effect of the Hg, Cs, and Yb atomic lines present in the spectrum reported by Kramer (1978b). The spectrum was analyzed to obtain molecular constants for several ytterbium monochloride states ($X^2\Sigma^+$: $T_e = 0$, $\omega_e = 290.0$, $\omega_e x_e = 0.45$; $A^2\Pi_{1/2}$: $T_e = 17,888.8$, $\omega_e = 311.0$, $\omega_e x_e = 0.45$; $A^2\Pi_{3/2}$: $T_e = 19,381.9$, $\omega_e = 312.5$, $\omega_e x_e = 0.55$; $B^2\Sigma^+$: $T_e = 19,939.9$, $\omega_e = 313.5$, $\omega_e x_e = 0.60$; $C^2\Pi_{1/2}$: $T_e = 22,842.6$, $\omega_e = 296.0$, $\omega_e x_e = 0.36$; $C^2\Pi_{3/2}$: $T_e = 23,385.5$, $\omega_e = 299.0$, $\omega_e x_e = 1.30$; $D^2\Sigma^+$: $T_e = 24,460.1$).

Newer data (Dickinson et al., 2001; Linton and Adam, 2001; Melville et al., 2000) on the molecular constants of YbCl have then been published. The high-resolution spectra obtained in these works allowed rotational levels of the lower (v = 0, 1, 2, 3) vibrational levels of the ground electronic state to be analyzed. The spectra were interpreted to determine B_e (and/or R_e), D_e , and α_1 values. These parameters for the $X^2\Sigma^+$ state were found to be $B_e = 9.350878 \times 10^{-2} \text{ cm}^{-1}$, $R_e = 2.4883 \text{ Å}$, $\alpha_1 = 3.8541 \times 10^{-4} \text{ cm}^{-1}$, and $D_e = 3.8581 \times 10^{-8} \text{ cm}^{-1}$ (Melville et al., 2000); $R_e = 2.4882877 \text{ Å}$ (Dickinson et al., 2001); $B_e = 9.35103 \times 10^{-2} \text{ cm}^{-1}$ and $\alpha_1 = 3.884 \times 10^{-4} \text{ cm}^{-1}$ (Linton and Adam, 2001). Dickinson et al. (2001) analyzed the spectra on the basis of the ω_e and $\omega_e x_e$ values reported by Lee and Zare(1977); these values were not reported by Melville et al. (2000). They can, however, be estimated from the equations that relate them to D_e and α_1 (Eqs. (31) and (32)). This gives $\omega_e = 291.15 \text{ cm}^{-1}$ and $\omega_e x_e = 0.92 \text{ cm}^{-1}$. The relationship $\Delta G_{1/2} = \omega_e - 2\omega_e x_e$ then yields $\Delta G_{1/2} = 289.31 \text{ cm}^{-1}$.

On the other hand, the approximate relationship between the atomization energy $\Delta_{\rm at}H^{\circ}(\rm YbCl,0)$ and vibrational constants ($\Delta_{\rm at}H^{\circ}(\rm YbCl,0)$) = $\omega_{\rm e}^2/4\omega_{\rm e}x_{\rm e} - 0.5\omega_{\rm e}$) results in the atomization energy of ytterbium monochloride being equal to ~23,100 cm⁻¹ (276 kJ/mol). According to Linton and Adam (2001), the fundamental vibrational frequency $\Delta G_{1/2}$ for the $X^2\Sigma^+$ state is 289.5386 cm⁻¹. Using the abovementioned definitions for $\Delta G_{1/2}$ and $\Delta_{\rm at}H^{\circ}$ (YbCl,0) and the $\Delta_{\rm at}H^{\circ}$ (YbCl,0) value, we arrive at the conclusion that the vibrational frequency and anharmonicity constant ($\omega_{\rm e} = 291.36 \text{ cm}^{-1}$ and $\omega_{\rm e}x_{\rm e} = 0.92 \text{ cm}^{-1}$) are close to those obtained by Melville et al. (2000).

In addition, the emission spectrum of lutetium monochloride was studied in the visible range (Kramer, 1978a). Two band systems were observed ($T_e = 20,844.9$, $\omega_e = 323.0$, $\omega_e x_e = 1.05$, and $T_e = 21,828.1$, $\omega_e = 369.3$, $\omega_e x_e = 1.79$ cm⁻¹). These results correspond to different low-lying states, probably to ${}^{1}\Sigma^{+}$ ($\omega_e = 350.6$ and $\omega_e x_e = 0.78$ cm⁻¹) and ${}^{1}\Delta$ ($\omega_e = 386.4$ and $\omega_e x_e = 1.76$ cm⁻¹).

In summary, analysis of the literature shows that data on the molecular constants of lanthanide monochlorides are very scarce. It follows that the thermodynamic functions for the whole series of these compounds can only be calculated using estimated constants.

Comparative analysis of the experimental data on ω_e and R_e for RF and RCl (for the pairs LaF/LaCl, YbF/YbCl, and LuF/LuCl) has shown the constancy of the $\omega_e(RF)/\omega_e(RCl)$ and $R_e(RF)/R_e(RCl)$ ratios for these compounds. This principle was instrumental in determining the $\omega_e(RCl)$ and $R_e(RCl)$ values from the $\omega_e(RF)$ and $R_e(RF)$ data in the series of lanthanide monochlorides. The resulting ω_e and R_e values obtained for lanthanide monochlorides are listed in Table 68.

The experimental $\omega_e x_e$ values for lanthanide monofluorides fairly accurately fall on the smooth curve of their dependence on vibrational frequencies ω_{e} . These constants were estimated for the RCl series on the assumption that, according to the $\Delta_{\rm at}H^{\circ}({\rm RX},0) = \omega_{\rm e}^2/4\omega_{\rm e}x_{\rm e} - 0.5\omega_{\rm e}$ expression, the ratio between the $\omega_e x_e$ constants of lanthanide monofluorides and monochlorides was directly proportional to the ratio between the squared frequencies ω_e and inversely proportional to the dissociation energies $\Delta_{at}H^{\circ}(RX,0)$. We were, however, unable to estimate $\omega_e x_e$ for RCl in the same way because the available data on dissociation energies of both RCl and RF are fragmentary and inconsistent. Next, we must take into account that the aforementioned expression allows the experimental $\omega_{\rm e}$ and $\omega_{\rm e} x_{\rm e}$ values to be correlated only if the dissociation energies are assigned values that strongly differ from the experimental ones (see the example of YbCl above). We assumed that the ratio between the dissociation energies of monochloride and monofluoride of the same lanthanide equals the value found from the ω_e and $\omega_e x_e$ molecular constants of LaCl (Xin and Klynning, 1994) and LaF (Bernard et al., 2000a), YbCl (Melville et al., 2000), and YbF (Uttam and Joshi, 1995). The $\omega_e x_e$ values for lanthanide monochlorides obtained using this ratio are listed in Table 68. The same table contains the D_e and α_1 constants calculated by Eqs. (31) and (32).

R	⊿G _{1/2}	ω _e	ω _e X _e	B _e	R _e (R—Cl)	$\alpha_1 \times 10^4$	$D_{ m e} imes 10^8$	References
La	339.6436	341.603	0.9797	0.096705	(2.498)	3.6399	3.119	Xin and Klynning (1994) ^a
	_	341.43	1.0014	0.0967011	_	3.64477	_	Rubinoff et al. (2003)
Ce	342.3	344.3	1.00	-	2.486	3.60	3.02	b
Pr	344.9	346.9	1.02	-	2.475	3.66	3.05	b
Nd	347.0	349.1	1.05	-	2.464	3.72	3.05	b
Pm	348.9	351.0	1.06	-	2.453	3.78	3.09	b
Sm	350.4	352.6	1.09	-	2.442	3.84	3.08	Ь
Eu	286.9	288.7	0.89	-	2.571	3.56	3.35	Ь
Gd	352.7	354.9	1.12	-	2.423	3.94	3.10	Ь
Tb	353.3	355.6	1.14	_	2.413	4.00	3.15	b
Dy	353.7	356.0	1.15	_	2.404	4.05	3.18	b
Ho	_	336.001	_	0.102186	_	_	_	Linton et al. (2005)
	353.8	356.1	1.17	_	2.396	4.10	3.22	Ь
Er	353.5	355.9	1.18	-	2.388	4.15	3.26	Ь
Tm	352.9	355.3	1.18	-	2.379	4.20	3.33	Ь
Yb	_	293.1	1.34	-	_	-	-	Gatterer et al. (1942)
		294.1	1.12					
		293.0	2.4					
	_	294.24	0.944	_	_	_	_	Lee and Zare (1977)
	_	292.3	0.89	_	_	_	_	Kramer (1978b)
	_	290.0	0.45	_	_	_	_	Uttam et al. (1997)
	_	_	_	0.093508	2.4883	3.85	3.85	Melville et al. (2000)

TABLE 68 Fundamental vibrational frequency $\Delta G_{1/2}$ and other molecular constants of the ground state of RCl^a

(continued)

TABLE 68 (continued)	
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R	⊿G _{1∕2}	ω _e	ω _e X _e	Be	R _e (R—Cl)	$\alpha_1 \times 10^4$	$D_{\rm e} imes 10^8$	References
	_	_	_	0.093498	2.4882877	_	_	Dickinson et al. (2001)
	289.5386	_	_	0.0935103	2.48733	3.884		Linton and Adam (2001)
	289.3	291.1	0.92	_	2.488	3.80	3.74	b
Lu	_	350.6/	0.78/	_	_	-	_	Kramer (1978a)
		386.4	1.76					
	_	337	1.048	0.102696	2.3732930	4.126	3.97	Cooke et al. (2005)
	351.0	353.4	1.19	_	2.366	4.28	3.41	b

^{*a*} All molecular constants are in cm⁻¹, except for the interatomic distance expressed in Å. The interatomic distance calculated from B_e is given between parentheses. ^{*b*} From polynomial functions; accepted in calculations of the thermodynamic functions.

Previous estimates (Chervonnyi and Chervonnaya, 2004d) of the molecular constants of RCl were performed without taking into account the experimental data for LaCl (Xin and Klynning, 1994) and HoCl (Dick and Linton, 2001). This gap was partially closed by Chervonnyi and Chervonnaya (2007e) who showed that the calculation of the reduced Gibbs energy from the molecular constants of the ground electronic state of LaCl (Xin and Klynning, 1994) leads to differences of ~0.2–0.4 J/(mol·K) from the previous results (Chervonnyi and Chervonnaya, 2004d). The main reason is that our estimates of ω_e (330.5 cm⁻¹) for LaCl (Chervonnyi and Chervonnaya, 2004d) turned out to be somewhat lower.

This circumstance served as a rationale for reestimating the molecular constants of RCl. Comparison with the initial results (Chervonnyi and Chervonnaya, 2004d) shows that the applied corrections are insignificant ($\leq 10 \text{ cm}^{-1}$ for ω_e and $\leq 0.05 \text{ cm}^{-1}$ for $\omega_e x_e$). It is worth noting that the results reported by Dick and Linton. (2001) are not consistent with our estimates, presumably for the same reasons as those assumed in the case of CeF.

10.2.3 Thermodynamic functions

The method for calculating the thermodynamic functions implies that the statistical sums over the rovibrational states of the ground and excited electronic states of the investigated molecules are the same. This allows us to estimate the contribution of the excited electronic states by applying the corresponding calculated correction (Gurvich et al., 1978–1984) to the contribution of the ground electronic state. This correction for the compounds under consideration was calculated by two methods. In the first method, the electronic excitation energies of the free R^+ ion from Martin et al. (1978) were used. Taking into account the temperature range of the calculation of the thermodynamic functions (298.15–3000 K), we restrict our consideration to the energy levels lower than 10,000 cm⁻¹.

In the second method, the excitation energies of the molecular electronic states for RX molecules (R = Ce–Yb and X = F, Cl) reported by Kaledin et al. (1996a) were used. For DyF, HoF, and TmF, the initial calculated energies (Kaledin et al., 1996a) of the low-lying states were subsequently revised (Kaledin et al., 1998). Excitation energies for low-lying levels of SmX were not reported by Kaledin et al. (1996a), but we obtained them directly from the authors. It is worth noting that Kaledin et al. (1996a, 1998) worked within the frame of the LFT. The molecular electronic states were considered as the levels of the free R⁺ ion perturbed by the field of the ligand X⁻. In calculations of molecular levels, the lowest-lying atomic multiplet state of the R⁺ ion was determined among a number of possible states for R⁺X⁻ (4fⁿ6s, 4fⁿ5d, 4fⁿ6p, 4fⁿ⁻¹6s², 4fⁿ⁻¹5d6s, 4fⁿ⁻¹5d6p, 4fⁿ⁻¹6s6p, and 4fⁿ⁺¹). Later, the data published

by Kaledin et al. (1996a) were reproduced for a limited range of excitation energies for RF by both Dai et al. (1998) and Ren et al. (1998).

The results of the calculation (Kaledin et al., 1996a) are presented in such a way that all levels lying in the range $2500-7500 \text{ cm}^{-1}$ are specified as the weighted value of their energy at 5000 cm^{-1} with the corresponding statistical weight (see Tables 69 and 70). The next range of excitation energies chosen by the authors ($7500-12,500 \text{ cm}^{-1}$) is characterized by the weighted value at 10,000 cm⁻¹ with the corresponding statistical weight.

RF	Electronic state energies (cm ⁻¹) with statistical weights between parentheses
CeF	0(2), 765(2), 1094(2), 1118(2), 1279(2), 1359(2), 1446(2), 1544(2), 1706 (2), 1817(2), 1956(2), 2049(2), 2208(2), 2442(2), 5000(174), 10,000 (242)
PrF	0(2), 933(2), 989(2), 1031(2), 1450(2), 1551(2), 1718(2), 1792(2), 1835(2), 1851(2), 1909(2), 1921(1), 2072(2), 2145(2), 2197(2), 2275(2), 2293(1), 2316(2), 2487(2), 5000(233), 10,000(601)
NdF	0(2), 49(2), 88(2), 240(2), 524(2), 544(2), 650(2), 937(2), 1022(2), 1331(2), 1352(2), 1412(2), 1482(2), 1550(2), 1551(2), 1669(2), 1765(2), 1854(2), 1855(2), 2186(2), 2365(2), 2381(2), 2425(2), 5000(496), 10,000(1016)
PmF	0(1), 93(2), 374(2), 529(1), 667(2), 854(2), 1064(2), 1164(1), 1300(2), 1457 (1), 1556(2), 1563(2), 1686(2), 1712(2), 1891(1), 1904(2), 2001(2), 2316 (2), 2426(1), 2454(2), 2500(2), 5000(771), 10,000(1544)
SmF	0(2), 269(2), 874(2), 1153(2), 1392(2), 1876(2), 1922(2), 2494(2), 2660(2), 2953(2), 3215(2), 3357(2), 4063(2), 4179(2), 4390(2), 4653(2), 4920(2), 5165(2), 5894(2), 5976(2), 6140(2), 6373(2), 6659(2), 6983(2), 7340(2), 8007(2), 8061(2), 8178(2), 8307(2), 8646(2), 9002(2), 9418(2), 9874(2), 5000(182), 10.000(376)
EuF	0(9), 1421(7)
GdF	0(8), 2285(7), 2386(2), 5000(72), 10,000(72)
TbF	0(2), 349(2), 697(2), 1034(2), 1338(2), 1567(2), 1656(1), 2353(2), 2550(2), 5000(817), 10,000(1723)
DyF	0(2), 472(2), 894(2), 1145(2), 1512(2), 1694(2), 1804(2), 1854(2), 2431(2), 5000(642), 10,000(1508)
HoF	0(2), 255(2), 410(2), 512(2), 591(2), 658(2), 711(2), 746(2), 759(1), 5000 (58), 10,000(597)
ErF	0(2), 22(2), 62(2), 119(2), 281(2), 411(2), 626(2), 5000(20), 10,000(202)
TmF	0(1), 30(2), 125(2), 300(2), 575(2), 968(2), 1473(2), 1629(1), 1696(2), 1944 (1), 2063(2), 2255(2), 5000(24), 10,000(38)
YbF	0(2), 5000(4), 10,000(4)

TABLE 69 Electronic states of RF(g) according to Kaledin et al. (1996a)^{*a*}

^a The excitation energies for SmF taken from the results of calculation presented by L.A. Kaledin and R.W. Field. The excitation energies for low-lying states of DyF, HoF, and TmF taken from Kaledin et al. (1998).

RCl	Electronic state energies (cm ⁻¹) with their statistical weights given within parentheses
CeCl	0(2), 652(2), 676(2), 678(2), 816(2), 963(2), 1027(2), 1172(2), 1248(2), 1737(2), 1872(2), 1890(2), 1924(2), 1975(2), 1982(2), 1984(2), 2111 (2), 2117(2), 2153(2), 2239(2), 2425(2), 2427(2), 2432(2), 2475(2), 5000(220), 10,000(248)
PrCl	0(2), 254(2), 389(2), 407(2), 446(2), 478(1), 624(2), 734(2), 808(2), 852 (2), 865(1), 1332(2), 1436(2), 1531(2), 1631(2), 1703(2), 1788(2), 1790 (2), 1834(2), 1843(2), 1880(2), 1883(1), 1895(2), 1967(2), 2017(2), 2035(1), 2242(2), 2343(2), 5000(281), 10,000(668)
NdCl	0(2), 52(2), 150(2), 342(2), 476(2), 505(2), 571(2), 699(2), 803(2), 1302 (2), 1318(2), 1357(2), 1429(2), 1482(2), 1520(2), 1534(2), 1590(2), 1623(2), 1698(2), 1889(2), 2339(2), 2352(2), 2380(2), 2430(2), 5000(340), 10,000(1226)
PmCl	0(1), 80(2), 325(2), 478(1), 569(2), 754(2), 852(2), 1075(1), 1140(2), 1331(2), 1386(2), 1407(2), 1466(1), 1536(2), 1762(2), 1804(1), 1846 (2), 1960(2), 2090(2), 2185(2), 2192(2), 2232(2), 2415(1), 2470(2), 5000(535), 10,000(1676)
SmCl ^a	0(2), 218(2), 708(2), 934(2), 1128(2), 1520(2), 1557(2), 2021(2), 2155(2), 2393(2), 2605(2), 2720(2), 3292(2), 3386(2), 3557(2), 3770(2), 3986 (2), 4185(2), 4776(2), 4842(2), 4975(2), 5164(2), 5395(2), 5658(2), 5947(2), 6488(2), 6531(2), 6626(2), 6731(2), 7005(2), 7294(2), 7631(2), 8000(2), 5000(182), 10.000(188)
EuCl	0(9), 1669(7)
GdCl	0(8), 1833(2), 1939(2), 2052(2), 2174(2), 2309(2), 2460(2), 5000(82), 10,000(74)
TbCl	0(2), 229(2), 444(2), 638(2), 796(2), 902(2), 939(1), 2088(2), 2221(2), 2340(2), 2432(2), 2490(2), 5000(1162), 10,000(1756)
DyCl	0(2), 102(2), 175(2), 229(2), 272(2), 292(2), 306(2), 333(2), 352(2), 361 (2), 527(2), 728(2), 875(2), 892(2), 983(2), 1019(2), 1057(2), 1111(2), 1112(2), 1155(2), 1170(2), 1187(2), 1198(2), 1209(2), 1221(2), 5000(754), 10,000(1372)
HoCl	0(2), 102(2), 177(2), 233(2), 277(2), 312(2), 337(2), 352(2), 357(1), 1810 (1), 1815(2), 1831(2), 1855(2), 1877(2), 1928(2), 1981(2), 2053(2), 2160(2), 2459(1), 2465(2), 2485(2), 5000(108), 10,000(655)
ErCl	0(1), 11(2), 33(2), 65(2), 108(2), 164(2), 239(2), 345(2), 5000(28), 10,000(270)
TmCl	0(1), 40(2), 97(1), 197(2), 243(1), 368(2), 474(2), 665(2), 816(2), 851(2), 875(2), 979(2), 1073(2), 1136(2), 1351(2), 1627(2), 5000(24), 10,000(41)
YbCl	0(2), 10,000(4)

 TABLE 70
 Electronic states in RCl(g) according to Kaledin et al. (1996a)

 $^{a}\,$ The excitation energies for SmCl are taken from the results of calculation presented by L.A. Kaledin and R.W. Field.

The use of these data in our calculations means that the range of excitation energies is extended up to $12,500 \text{ cm}^{-1}$.

The calculations of the thermodynamic functions are summarized in Tables A9–A13 in Appendix.

The differences observed for some molecular constants after applying the approximation procedure to the available experimental data are discussed above. Taking into account their low values, we assume that errors on the theoretically estimated values are ± 0.005 Å for the interatomic distances, ± 5 cm⁻¹ for the vibrational constants, and ± 0.3 cm⁻¹ for the anharmonicity constants. As a result, the error on the calculated rovibrational contribution is rather small and is not crucial. The major source of error for the thermodynamic functions is the uncertainty in the excitation energy.

The contribution made by the correction for electronic excitation is very noticeable for the class of compounds under consideration. Figures 41 and 42 show the correction value in the entire range of calculation temperatures for RF. For RCl, this correction is equal or close to that



FIGURE 41 Electronic contribution to the thermodynamic functions of RF. Calculation from the excitation energies of R^+ ions (R = La-Lu). Reproduced from Chervonnyi and Chervonnaya (2007d) with permission from Pleiades Publishing, Ltd.



FIGURE 42 Electronic contribution to the thermodynamic functions of RF. Calculation from the excitation energies of RF (R = Ce-Yb). Reproduced from Chervonnyi and Chervonnaya (2007d) with permission from Pleiades Publishing, Ltd.

shown in Figures 41 and 42. Let us note the evident difference between these figures. The curves for the 4f elements shown in Figure 41 are double-humped within the entire temperature range. Figure 42 shows how these curves change (especially for heavy lanthanide compounds) when the electronic contribution is calculated from the data reported by Kaledin et al. (1996a, 1998).

To clearly show the differences in thermodynamic functions that arises due to the use of different methods of calculation of the electronic component, Tables 71 and 72 present the reduced Gibbs energies (third and fourth columns) and enthalpies (fifth and sixth columns) at three temperatures. As is known, these parameters are used in calculations of equilibria by the third and second laws of thermodynamics, respectively. The seventh column in these tables presents the differences (δ_1) between the values in the third and fourth columns, and the eighth column presents the differences (δ_2) between the values of the fifth and sixth columns.

The data in Tables 71 and 72 demonstrate that δ_1 and δ_2 are zero (or close to zero) only for EuX and YbX. This means that the electronic excitation energies are close for molecules and ions. Indeed, EuX has

R	Т (К)	-[G°(T) -	- <i>H</i> °(0)]∕ <i>T</i>	$H^{\circ}(T) - H^{\circ}(0)$		δ_1	δ_2
1	2	3	4	5	6	7	8
Ce	298.15	225.036	213.799	9.499	9.369	11.237	0.130
	1500	287.905	280.325	71.828	73.147	7.580	-1.319
	2000	301.986	294.653	99.650	101.570	7.333	-1.920
Pr	298.15	227.047	213.664	9.815	9.408	13.383	0.407
	1500	287.677	281.091	64.414	76.397	6.586	-11.983
	2000	300.372	296.057	90.649	105.980	4.315	-15.331
Nd	298.15	225.969	222.731	9.753	9.957	3.238	-0.204
	1500	287.267	287.208	64.853	71.915	0.059	-7.062
	2000	299.952	301.587	89.831	103.749	-1.635	-13.918
Pm	298.15	222.507	216.440	9.992	10.795	6.067	-0.803
	1500	285.551	285.638	65.940	81.849	-0.087	-15.909
	2000	298.332	301.856	89.581	114.986	-3.524	-25.405
Sm	298.15	217.130	216.062	10.684	10.012	1.068	0.672
	1500	283.562	278.162	68.339	64.844	5.400	3.495
	2000	296.734	290.756	91.779	88.493	5.978	3.286
Eu	298.15	227.770	227.781	9.346	9.359	-0.011	-0.013
	1500	283.597	283.895	56.674	56.784	-0.298	-0.110
	2000	294.568	294.867	76.864	76.747	-0.299	0.117
Gd	298.15	226.629	225.873	10.347	9.006	0.756	1.341
	1500	289.192	280.447	63.306	58.573	8.745	4.733
	2000	301.499	292.206	86.655	85.635	9.293	1.020
Tb	298.15	232.247	216.097	9.072	10.081	16.150	-1.009
	1500	289.408	283.913	62.075	87.949	5.495	-25.874
	2000	301.687	301.248	87.863	121.678	0.439	-33.815
Dy	298.15	232.984	215.534	9.258	9.825	17.450	-0.567
2	1500	289.342	282.988	56.945	86.073	6.354	-29.128
	2000	300.407	299.998	77.993	119.920	0.409	-41.927
Но	298.15	232.829	219.038	9.387	11.181	13.791	-1.794
	1500	289.320	282.650	56.029	61.243	6.670	-5.214
	2000	300.166	294.760	76.181	87.452	5.406	-11.271
Er	298.15	231.808	225.569	9.575	10.082	6.239	-0.507
	1500	288.279	283.081	55.538	56.291	5.198	-0.753
	2000	299.043	294.083	75.688	78.284	4.960	-2.596
Tm	298.15	229.220	221.503	9.660	10.267	7.717	-0.607
	1500	284.911	281.868	54.336	60.682	3.043	-6.346
	2000	295.403	293.654	73.454	82.968	1.749	-9.514
Yb	298.15	216.239	216.240	9.279	9.278	0	0
	1500	270.731	270.869	53.875	54.864	-0.138	-0.989
	2000	281.144	281.599	72.937	76.198	-0.455	-3.261

TABLE 71 Selected values of the thermodynamic functions for RF $(gas)^a$

^{*a*} Data in the third and fifth columns were obtained by taking into account the electronic excitation energies for the free La⁺ ion, and the data in the fourth and sixth columns were obtained by taking into account the electronic excitation energies of RF molecules. The reduced Gibbs energy $-[G^{\circ}(T) - H^{\circ}(0)]/T$ is expressed in J/(mol·K), while the enthalpy is in kJ/mol.

R	Т (К)	–[G°(T) – H°(0)]∕T		$H^{\circ}(T) - H^{\circ}(0)$		δ_1	δ_2
1	2	3	4	5	6	7	8
Ce	298.15	235.379	225.070	10.017	10.633	10.309	-0.616
	1000	281.543	276.992	44.778	47.085	4.551	-2.307
	1500	300.551	296.493	73.134	73.702	4.058	-0.568
Pr	298.15	237.380	229.020	10.333	11.822	8.360	-1.489
	1000	283.142	280.663	41.050	44.689	2.479	-3.639
	1500	300.329	299.240	65.736	70.745	1.089	-5.009
Nd	298.15	236.292	232.428	10.270	11.015	3.864	-0.745
	1000	282.500	281.472	41.818	43.447	1.028	-1.629
	1500	299.927	299.755	66.194	70.576	0.172	-4.382
Pm	298.15	232.815	227.646	10.514	10.876	5.169	-0.362
	1000	280.362	278.469	43.087	46.360	1.893	-3.273
	1500	298.220	298.345	67.294	77.837	-0.125	-10.543
Sm	298.15	227.428	227.077	11.206	10.275	0.351	0.931
	1000	277.624	274.637	45.137	43.282	2.987	1.855
	1500	296.235	293.044	69.710	71.580	3.191	-1.870
Eu	298.15	238.424	238.430	9.889	9.885	-0.006	0.004
	1000	281.028	281.029	37.417	37.416	0	0
	1500	296.452	296.453	57.886	57.882	0	0.004
Gd	298.15	236.902	236.139	10.873	9.534	0.763	1.339
	1000	284.668	278.125	41.733	37.851	6.543	3.882
	1500	301.872	294.203	64.702	62.505	7.669	2.197
Tb	298.15	242.511	228.209	9.602	11.140	14.302	-1.538
	1000	285.616	277.502	39.087	47.375	8.114	-8.288
	1500	302.101	299.352	63.487	89.431	2.749	-25.944
Dy	298.15	243.257	236.075	9.780	12.011	7.182	-2.231
-	1000	286.465	286.240	37.928	43.689	0.225	-5.761
	1500	302.041	305.095	58.365	75.324	-3.054	- 16.959
Ho	298.15	243.090	234.928	9.920	11.542	8.162	-1.622
	1000	286.619	282.286	37.728	40.453	4.333	-2.725
	1500	302.034	299.118	57.463	64.232	2.916	-6.769
Er	298.15	242.072	237.730	10.107	10.625	4.342	-0.518
	1000	285.729	281.764	37.398	37.141	3.965	0.257
	1500	301.005	296.992	56.983	57.239	4.013	-0.256
Tm	298.15	239.481	232.967	10.197	11.366	6.514	-1.169
	1000	282.661	281.733	36.733	41.209	0.928	-4.476
	1500	297.649	298.433	55.789	61.771	-0.784	-5.982
Yb	298.15	226.876	226.871	9.835	9.841	0.005	-0.006
	1000	268.882	268.882	36.106	36.106	0	0
	1500	283.662	283.663	55.164	55.181	0	0

TABLE 72 Selected values of the thermodynamic functions for RCl (gas)^{*a*}

^{*a*} Data in the third and fifth columns were obtained taking into account the electronic excitation energies for the free La⁺ ion, and the data in the fourth and sixth columns were obtained taking into account the electronic excitation energies of RCl molecules. The reduced Gibbs energy $-[G^{\circ}(T) - H^{\circ}(0)]/T$ is expressed in J/(mol•K), while the enthalpy is in kJ/mol.
high-multiplicity states (${}^9\Sigma^-$ with $T_e = 0$ and ${}^7\Sigma^-$ with $T_e = \sim 1500 \text{ cm}^{-1}$), and the free Eu⁺ ion has the ground-state term 9S_4 (stable electronic configuration [Xe]4f⁷6s¹, which is not split in the ligand field) and two excited states at 1669.21 (7) and 9923.00 (5) cm⁻¹ (the statistical weights of the states are given between parentheses). The ground-state terms of YbX (${}^2\Sigma^+$) and Yb⁺ (${}^2S_{1/2}$) mean that their statistical weights are the same. The difference is that the electronic states with energy 10,000 cm⁻¹ (statistical weight, 4) are taken into account in Kaledin et al. (1996a), which is responsible for an insignificant addition to the electronic component of the thermodynamic functions.

For most of the other lanthanide monohalides, maximal δ_1 values are observed even at 298.15 K (Tables 71 and 72). This is mainly due to a change in the behavior of the ground-state term in the ligand field. The calculation based on the excitation energies of free ions R⁺ implies that their terms are not split in RX molecules. However, as follows from data reported by Kaledin et al. (1996a, 1998), Dai et al. (1998), and Ren et al. (1998), the ground-state term, which is not always coinciding with the corresponding term of the free ion R⁺ (Cao and Dolg, 2002; Martin et al., 1978), is split in the ligand field.

The first calculations of the thermodynamic functions of RX₃ molecules were performed using their low-lying excited states obtained from the excitation energies for the free R^{3+} ions (Myers and Graves, 1977a). We justified the use of Morrison and Leavitt (1982) data for the R^{3+} ions in crystals as a way of taking into account the effect of the ligand field on the central atom in the calculations of the thermodynamic functions of RCl₃ (Chervonnyi and Chervonnaya, 2004g). It should be emphasized that the data of Morrison and Leavitt (1982) are characterized by a rather small splitting of the ground-state term. The weighted average value of the excitation energies for it is, as a rule, no more than 100 cm⁻¹. This model has also been applied to RCl₂ molecules (Chervonnyi and Chervonnaya, 2003). The splitting of the ground-state term for these compounds turns out to be even smaller.

The applicability of the data on 4f elements intercalated into different crystal lattices for estimating this splitting from available experimental results was demonstrated by Chervonnyi and Chervonnaya (2003, 2004c,g). Nevertheless, such a procedure is only an approximation that slightly improves the quality of the thermodynamic functions as compared to the approach based on the data for the free ion.

More reliable information on the excited states could be provided by quantum-chemical calculations. Such calculations have been performed for some trihalides (Tsuchia et al., 1999); however, they deal with the D_{3h} rather than C_{3v} structure of the corresponding molecules. Therefore, we did not use these data in our calculations of the thermodynamic functions for RX₃ but compared them with our previous results

(Chervonnyi and Chervonnaya, 2003, 2004c,g). It turned out that the range of changes in the energies of low-lying states reported by Tsuchia et al. (1999) is only slightly higher. As a result, the reduced Gibbs energy is lower than in the calculation with inclusion of the Stark splitting of the ground-state term in the ligand field. However, the difference is within the error of the experimental determinations of the thermodynamic functions.

Comparison of the ground-state term splitting in RX_3 and RX_2 allows us to assume that it should be insignificant, typically on the order of a few tens of cm⁻¹ or even less. In the absence of data on the character of splitting (or a method for its estimation), it can be ignored. In contrast to this, the data from several authors (Dai et al., 1998; Kaledin et al., 1996a 1998; Ren et al., 1998) show that the weighted average values of the ground-state term splitting can be as large as ~1000 cm⁻¹. This difference was our basic motivation for using two methods of calculation of the thermodynamic functions of RX.

The influence of the low-lying state energies on the thermodynamic functions is exemplified by the calculation of the electronic contribution to the reduced Gibbs energy and enthalpy of HoF (see Figures 43 and 44). As can be seen, the calculations differ significantly depending on the method used.

Based on the above discussion, we have no good reasons for choosing between the first and second methods of calculation of the contribution of



FIGURE 43 Electronic contribution to the reduced Gibbs energy. Calculated from the excitation energies of (1) HoF and (2) from the excitation energies of free ions Ho⁺.



FIGURE 44 Electronic contribution to the enthalpy. Calculated from the excitation energies of (1) HoF and (2) from the excitation energies of free ions Ho⁺.

the excited electronic states, and we are still unable to assess the total error in the thermodynamic functions suggested in this work. We hope that this issue will be made clearer after further examination of the enthalpies of reactions and the enthalpies of atomization obtained by processing experimental data.

11. THERMODYNAMIC PROPERTIES OF RCL, RCL^+ , RF, RF^+ , AND RF_2

The method of calculation of thermodynamic functions for gaseous RX (R = La-Lu and X = F, Cl) implies that the statistical sums over the rovibrational levels of the ground and excited electronic states of the molecules are equal. This allows one to consider the contribution of excited electronic states in the form of a correction to the contribution of the ground state. As follows from the previous section, due to different values of these corrections, some sets of final data for certain RX compounds noticeably differ from one another. At real temperatures, the difference in reduced Gibbs energy is as large as 4–7 J/(mol·K) for some monochlorides and even larger, about 5–9 J/(mol·K), for some monofluorides.

In this context, it is of interest to use the thermodynamic functions described in previous sections for processing the experimental data on

high-temperature heterogeneous and homogeneous equilibria involving the molecules under consideration. The aims of this procedure are first to determine which of the methods of calculation of the correction for electronic excited states of the monohalides affords the most adequate description of thermodynamic functions and, second, to estimate characteristic parameters for unstudied compounds, taking into account that relevant experimental data are available only for some of the lanthanide compounds discussed in this section.

This can be attained by comparison of the enthalpies of reactions calculated by the second and third laws, $\Delta_r H^{\circ}(0, \text{ II law})$ and $\Delta_r H^{\circ}(0, \text{ III law})$, under standard conditions and the enthalpies of atomization $\Delta_{at}H^{\circ}(0, \text{ III law})$ and $\Delta_{at}H^{\circ}(0, \text{ III law})$ calculated from these data for gaseous RX and RF₂. The latter parameters change predictably along the lanthanide series. It is worth noting that available experimental data do not often lead to agreement between $\Delta_r H^{\circ}(0, \text{ III law})$ and $\Delta_r H^{\circ}(0, \text{ III law})$. As a rule, calculations by the third law afford more precise results with a smaller error. However, we think that such a comparison will lead to interesting conclusions due to differences in $(H^{\circ}(T) - H^{\circ}(0))$ values of the thermodynamic functions for RX.

Additional interest for such data processing is stirred by the fact that the experimental data (Kleinschmidt et al., 1981; Zmbov and Margrave, 1966a,c, 1967a, 1968) have not been used for calculating the enthalpies of reactions by the third laws due to the absence of the required thermodynamic functions.

11.1 Equilibrium constants and enthalpies of reactions involving RF, RF_2, and RCl

Gaseous lower lanthanide (I and II) fluorides and chlorides have been obtained in detectable amounts by different methods. One synthetic way for instance is to heat BaF_2 -Nd and RF_3 -R (R = Nd, Sm, Eu, Gd, Dy, Ho, and Er) mixtures in a Knudsen effusion cell (Zmbov and Margrave, 1966a,c, 1967a).

Hildenbrand and Lau (1995) have obtained samarium and europium fluorides by reacting a mixture of gaseous CaF_2 and RF_3 with boron or by evaporating CaF_2 – R_2O_3 mixtures. Additionally, gaseous thulium fluorides were synthesized by heating a TmF_3 – CaF_2 –B mixture to required temperatures (Hildenbrand and Lau, 1995). The same authors also obtained lanthanum fluorides by the reaction of lanthanum metal with barium difluoride or with gaseous sulfur hexafluoride delivered to the lanthanum evaporation zone.

The conditions for the predominant formation of EuF_2 and EuF_3 in the gas phase were worked out by Kleinschmidt et al. (1981) by evaporating europium trifluoride from a platinum or graphite container containing a

tungsten wire; to stabilize the partial pressures of the gaseous tungstencontaining components, gaseous tungsten hexafluoride was additionally fed to the reaction zone.

Chlorides have been obtained by heating BaCl₂-R mixtures (Chervonnyi, 1977a,b; Chervonnyi and Chervonnaya, 2004a,b,e,f, 2005b). This method of synthesis of low-valence lanthanide chlorides was used for the first time by Chervonnyi (1977a,b); however, the results obtained at rather high ionizing electron energy were suitable for reliable determination of equilibrium constants only for gas-phase reactions involving lanthanide dichlorides (Chervonnyi and Chervonnaya, 2008b). Monoand dichlorides have also been prepared by the reaction of lanthanide atoms with molecular chlorine in an argon matrix (Loktyushina et al., 1984). Alternatively, Sapegin (1984) heated R-EuCl₂ or R-RCl₂ mixtures to measure the ionization and appearance energies of ions induced by the electron impact of lower valence chlorides.

In addition to the above high-temperature gas-phase reactions, direct interaction of lanthanide vapors with molecular fluorine was shown to yield monofluorides when studying the chemiluminescence of the products of the reaction of samarium, europium, or ytterbium vapor with F₂ in argon (Dickson and Zare, 1975; Yokozeki and Menzinger, 1976). On the other hand, heating a R-EuCl₂ mixture was also used by Chervonnyi (1977a,b) for studying specific chlorides. However, in this work, we comprehensively survey only the results of those experimental works in which the equilibrium constants of the reactions involved were measured. The method of measurement of these constants and required instrumentation were described in detail in Zmbov and Margrave (1966a,c, 1967a, 1968), Kleinschmidt et al. (1981), Hildenbrand and Lau (1995), and Chervonnyi and Chervonnaya (2004a,b,e,f, 2005b) and are not considered in this work.

Taking into account the fact that major errors in the measurement of equilibrium constants (see, for instance, Hildenbrand, 1995) are caused by the uncertainty with which ionization thresholds are determined for each component, we have given a special attention to this parameter in the case of some monochlorides (R = La, Sm, Eu, and Yb; Chervonnyi and Chervonnaya, 2004a,b,e,f, 2005b). Information on the other IEs of RCl and RF (IE(RX)) is presented below while discussing the enthalpies of atomization $\Delta_{at}H^{\circ}(0)$ of RX⁺ ions.

Thirty reactions involving lanthanide fluorides with different valence states (RF, RF₂, and RF₃) and 14 reactions involving the corresponding chlorides have been studied so far. Experimental data on these reactions, as well as the results of processing them by the second and third law methods, are listed in Tables 73 and 74.

The difference between the data in the sixth and seventh columns from those in the eighth and ninth columns is that the former were calculated from the thermodynamic functions in which the contribution of the

Reaction	No.	т (К)	A	В	∆ _r H°(0, III law) ^a	∆ _r H°(0, II law) ^a	∆ _r H°(0, III law) ^b	∆ _r H°(0, II law) ^b	References
1	2	3	4	5	6	7	8	9	10
$La + LaF_2 = 2LaF$	(1)	2008–2270	$\begin{array}{c} 0.101 \pm \\ 0.046 \end{array}$	1167 ± 99	15.5 ± 0.5	$-18.7\pm$ 1.9	$-15.7\pm$ 0.5	-30.1 ± 1.9	С
$Ba + LaF_2 = BaF + LaF$	(2)	1917–2131	1.499 ± 0.055	$\begin{array}{r}-3803 \pm \\113\end{array}$	63.4 ± 0.5	74.9 ± 2.2	48.2 ± 0.8	69.3 ± 2.2	с
LaF + Ba = BaF + La	(3)	-	-	-	51.7	-	66.9	-	с
Ba + NdF = BaF + Nd	(4)	1364–1512	-0.042 ± 0.117	480 ± 167	-0.4 ± 0.4	-5.7 ± 3.6	0.0 ± 0.4	0.6 ± 3.6	d
$Ba + NdF_2 = BaF + NdF$	(5)	1354–1477	1.563 ± 0.289	$-1376~\pm$ 407	16.0 ± 0.6	27.3 ± 7.1	15.5 ± 0.6	21.2 ± 7.1	d
2BaF + Nd = $2Ba + NdF_2$	(6)	1363–1511	-1.334 ± 0.289	559 ± 418	$^{-14.1} \pm 0.7$	-18.1 ± 3.8	-14.1 ± 0.7	-18.1 ± 3.8	d
3BaF + Nd = $3Ba + NdF_3$	(7)	1364–1512	-8.477 ± 0.739	$11,\!138 \pm 1052$	$^{-80.8\pm}_{-5.6}$	$^{-194.4}_{-20.9}$	$^{-80.8}_{-5.6}$	-194.4 ± 20.9	d
$NdF_3 + 2Nd =$ 3NdF	(8)	1411–1514	$\begin{array}{r} 4.877 \pm \\ 0.371 \end{array}$	-7760 ± 539	90.1 ± 1.7	$\begin{array}{c} 148.0 \pm \\ 10.5 \end{array}$	89.2 ± 1.7	128.4 ± 10.5	d
$2NdF_3 + Nd = 3NdF_2$	(9)	1412–1514	3.935 ± 0.347	-9337 ± 508	$\begin{array}{c} 148.7 \pm \\ 1.2 \end{array}$	$\begin{array}{c} 184.7 \pm \\ 11.7 \end{array}$	$\begin{array}{c} 148.7 \pm \\ 1.2 \end{array}$	184.7 ± 11.7	d
Sm + CaF = SmF + Ca	(10)	1729–2191	-0.398 ± 0.068	$\begin{array}{c} 1800 \pm \\ 127 \end{array}$	-25.7 ± 1.7	$-36.9\pm$ 2.5	$-37.1\pm$ 1.7	-33.6 ± 2.5	е
$\begin{array}{l} SmF+CaF=\\ SmF_2+Ca \end{array}$	(11)	1448–1643	-1.171 ± 0.188	$\begin{array}{c} 1449 \pm \\ 291 \end{array}$	$\begin{array}{c}-24.8\pm\\1.0\end{array}$	$\begin{array}{r}-32.4\pm\\5.9\end{array}$	$\begin{array}{c} -16.2 \pm \\ 1.0 \end{array}$	-35.9 ± 5.9	е

TABLE 73 Equilibrium constants (log $K_p^{\circ} = A + B/T$) and enthalpies of gas-phase reactions involving lanthanide fluorides (kJ/mol)

(continued)

TABLE 73	(continued)	
	(continued)	

Reaction	No.	Т (К)	A	В	∆ _r H°(0, III law) ^a	∆ _r H°(0, II law) ^a	$\Delta_{r} \mathcal{H}^{\circ}(0, III law)^{b}$	∆ _r H°(0, II law) ^b	References
1	2	3	4	5	6	7	8	9	10
$SmF + SmF_3 = 2SmF_2$	(12)	1532–1673	$\begin{array}{c} 1.016 \pm \\ 0.085 \end{array}$	-634 ± 135	6.0 ± 1.0	15.2 ± 2.8	14.9 ± 1.0	11.6 ± 2.8	е
Eu + CaF = EuF + Ca	(13)	1618–1785	-0.215 ± 0.118	776 ± 199	$^{-11.5}_{-0.5}$	$-15.6\pm$ 4.3	-11.0 ± 0.5	-15.6 ± 4.3	е
Eu + CaF = EuF + Ca	(13)	1878–2014	$\begin{array}{c} 0.007 \pm \\ 0.256 \end{array}$	584 ± 409	$^{-15.1}_{-0.7}$	$^{-19.5}_{-10.5}$	-14.5 ± 0.7	-19.4 ± 10.5	е
$EuF + CaF = EuF_2 + Ca$	(14)	1824–2014	-1.132 ± 0.190	537 ± 365	-9.9 ± 0.7	-13.4 ± 7.6	$-10.5\pm$ 0.7	-13.5 ± 7.6	е
$\begin{array}{l} EuF_3+WF_4=\\ EuF_2+WF_5 \end{array}$	(15)	1443–1528	$\begin{array}{c} 0.625 \pm \\ 0.092 \end{array}$	-2798 ± 142	20.8 ± 1.9	67.9 ± 2.9	20.8 ± 1.9	67.9 ± 2.9	е
2HoF + GdF = $2Ho + GdF_3$	(16)	1369–1491	-2.614 ± 0.342	$\begin{array}{r} 5969 \pm \\ 487 \end{array}$	-125.9 ± 0.7	-137.8 ± 9.3	-94.2 ± 0.7	-133.4 ± 9.3	f
$GdF + HoF_2 = GdF_2 + HoF$	(17)	1374–1483	0.114 ± 0.336	854 ± 478	-14.2 ± 0.6	$-26.5\pm$ 4.6	-11.7 ± 0.6	-36.2 ± 4.6	f
$\begin{array}{l} GdF_2 + HoF = \\ GdF_3 + Ho \end{array}$	(18)	1358–1490	-1.440 ± 0.460	$\begin{array}{r} 3359 \pm \\ 654 \end{array}$	$^{-85.3}_{-1.4}$	$^{-90.7} \pm 12.5$	-75.5 ± 1.4	-86.1 ± 4.6	f
Ho + DyF = HoF + Dy	(19)	1400–1520	-0.145 ± 0.209	814 ± 305	-11.0 ± 0.5	-11.0 ± 5.0	-10.8 ± 0.5	11.8 ± 5.0	8
Ho + SmF = HoF + Sm	(20)	1355–1450	$\begin{array}{c} 0.393 \pm \\ 0.364 \end{array}$	-472 ± 510	-1.8 ± 0.6	10.4 ± 9.8	-4.1 ± 0.6	2.5 ± 5.0	f
Ho + EuF = HoF + Eu	(21)	1238–1418	-1.117 ± 0.116	724 ± 152	12.9 ± 1.2	-14.0 ± 2.9	3.2 ± 1.2	-17.9 ± 2.9	f

3HoF = 2Ho	(22)	1316-1424	$-1.181~\pm$	$3377 \pm$	-108.4 \pm	$-96.6 \pm$	$-79.8~\pm$	-83.5 ± 9.7	8
$+ HoF_3$			0.373	509	1.3	9.7	1.3		
$HoF_2 + Ho =$	(23)	1316-1425	$1.055~\pm$	$-1454~\pm$	27.2 ± 0.8	15.0 ± 9.6	8.2 ± 0.8	6.3 ± 9.6	8
2HoF			0.375	509					
$3\text{HoF}_2 = 2\text{HoF}_3$	(24)	1322-1423	$-0.567 \pm$	$4411~\pm$	$-138.0~\pm$	$-82.4~\pm$	$-138.0~\pm$	-82.4 ± 11.9	8
+ Ho			0.454	621	1.4	11.9	1.4		
HoF + Er = Ho	(25)	1404–1519	$-0.036~\pm$	950 ± 496	$-16.5~\pm$	$-24.4~\pm$	$-14.2~\pm$	-20.2 ± 9.5	8
$+ \mathrm{ErF}$			0.341		0.8	9.5	0.8		
$HoF_2 + Er = Ho$	(26)	1419–1520	$-0.446~\pm$	1343 \pm	$-16.1 \pm$	$-20.5~\pm$	$-16.1~\pm$	-20.5 ± 5.8	8
$+ ErF_2$			0.213	313	0.4	5.8	0.4		
$HoF_3 + Er = Ho$	(27)	1404–1520	$0.098~\pm$	1045 \pm	$-22.4~\pm$	$-21.5 \pm$	$-22.4~\pm$	-21.5 ± 6.7	8
$+ ErF_3$			0.345	502	0.9	6.7	0.9		
Tm + CaF =	(28)	1445–1952	$0.079~\pm$	$-1149 \pm$	15.5 ± 0.9	20.7 ± 1.0	11.3 ± 0.9	13.1 ± 1.0	е
TmF + Ca			0.030	50					
TmF + CaF =	(29)	1447–1926	$-0.417~\pm$	1201 ± 68	$-51.0 \pm$	$-30.4~\pm$	$-46.7~\pm$	-22.9 ± 1.4	е
$TmF_2 + Ca$			0.042		2.4	1.4	2.4		
$TmF + TmF_3$	(30)	1447–1564	1.301 \pm	$-2951 \pm$	34.7 ± 1.0	61.5 ± 9.1	39.2 ± 1.0	67.9 ± 9.1	е
$= 2TmF_2$			0.293	441					

^a Calculated using the thermodynamic functions in which the electronic component was determined from the excitation energies of R⁺ ions.
^b Calculated using the thermodynamic functions in which the electronic component was determined from the excitation energies of RF.
^c Hildenbrand and Lau (1995).
^d Zmbov and Margrave (1966a).
^e Kleinschmidt et al. (1981).
^f Zmbov and Margrave (1967a).
^g Zmbov and Margrave (1966c).

Reaction	No.	<i>Т</i> (К)	А	В	$\Delta_{ m r} {\cal H}^{\circ}$ (0, III law) a	$\Delta_{ m r} {\it H}^{\circ}$ (0, II law) a	$\Delta_{ m r} {\it H}^{\circ}$ (0, III law) ^b	$\Delta_{ m r} {\it H}^{\circ}$ (0, II law) ^b	References
1	2	3	4	5	6	7	8	9	10
BaCl + La =	(1)	1380-	$-0.417~\pm$	$3375 \pm$	$-60.1 \pm$	$-65.5 \pm$	$-66.9 \pm$	$-69.0 \pm$	С
Ba + LaCl		1446	0.293	414	0.4	7.9	0.4	7.9	
BaCl + Ce =	(2)	1365-	$-0.663~\pm$	$2810~\pm$	$-50.1 \pm$	$-55.8 \pm$	$-55.9~\pm$	$-56.7 \pm$	d
Ba + CeCl		1440	0.225	315	0.4	5.5	0.4	5.5	
BaCl + Pr =	(3)	1365-	$-0.237 \pm$	$1540~\pm$	$-30.2 \pm$	$-31.3 \pm$	$-32.0 \pm$	$-36.1 \pm$	d
Ba + PrCl		1470	0.132	187	0.4	3.6	0.4	3.6	
BaCl + Nd =	(4)	1279–	$-0.218~\pm$	$319 \pm$	$-8.2~\pm$	$-8.6~\pm$	$-8.8~\pm$	$-11.8~\pm$	d
Ba + NdCl		1420	0.086	115	0.4	2.2	0.4	2.2	
BaCl + Sm =	(5)	1090-	$-0.158~\pm$	$-621 \pm$	8.6 ± 0.2	11.6 \pm	5.0 ± 0.2	12.9 \pm	е
Ba + SmCl		1175	0.077	88		1.7		1.7	
BaCl + Eu	(6)	1328-	$-0.046~\pm$	-1367	$20.9~\pm$	$23.8~\pm$	$20.9~\pm$	$23.8~\pm$	e,f
= Ba +		1400	0.353	± 481	0.6	9.2	0.6	9.2	
EuCl									
BaCl + Gd =	(7)	1360-	$-0.563~\pm$	$1580~\pm$	$-26.9~\pm$	$-32.5 \pm$	$-37.7~\pm$	$-29.8~\pm$	d
Ba + GdCl		1488	0.175	248	0.7	4.4	0.7	4.4	
BaCl + Tb =	(8)	1416–	$-0.883~\pm$	1021 \pm	$-17.1~\pm$	$-20.0~\pm$	-21.5 \pm	$-45.4~\pm$	d
Ba + TbCl		1550	0.098	145	0.4	2.8	0.4	2.8	
BaCl + Dy =	(9)	1229–	$-0.251~\pm$	-1596	$28.3~\pm$	$28.5~\pm$	$30.5 \pm$	17.0 \pm	d
Ba + DyCl		1376	0.222	± 288	1.1	5.5	1.1	5.5	
BaCl + Ho =	(10)	1270-	$-0.282~\pm$	-1172	$21.6~\pm$	$20.6~\pm$	17.1 \pm	15.4 \pm	d
Ba + HoCl		1420	0.101	\pm 135	0.5	2.6	0.5	2.6	

TABLE 74 Equilibrium constants (log $K_p^{\circ} = A + B/T$) and enthalpies of gas-phase reactions involving lanthanide monochlorides (kJ/mol)

BaCl + Er =	(11)	1274–	$-0.234~\pm$	$-638~\pm$	10.9 \pm	10.9 \pm	5.6 ± 0.4	11.0 \pm	d
Ba + ErCl		1396	0.085	114	0.4	2.2		2.2	
BaCl + Tm =	(12)	1304-	$-0.166~\pm$	-3054	56.3 \pm	57.8 \pm	56.8 \pm	52.3 \pm	d
Ba + TmCl		1418	0.328	\pm 447	1.1	8.6	1.1	8.6	
BaCl + Yb =	(13)	1140-	$-0.106~\pm$	-4097	78.8 \pm	78.5 \pm	78.8 \pm	78.5 \pm	е
Ba + YbCl		1225	0.071	\pm 84	0.2	1.6	0.2	1.6	
BaCl + Lu =	(14)	1316-	$-1.368~\pm$	1391 \pm	$-21.9~\pm$	$-22.2~\pm$	$-21.9~\pm$	$-22.2~\pm$	d
Ba + LuCl		1446	0.088	121	0.4	2.3	0.4	2.3	

^a Calculated using the thermodynamic functions in which the electronic component was determined from the excitation energies of R⁺ ions.
 ^b Calculated using the thermodynamic functions in which the electronic component was determined from the excitation energies of RCI.
 ^c Chervonnyi and Chervonnaya (2004b).
 ^d Chervonnyi and Chervonnaya (2007f).
 ^e Chervonnyi and Chervonnaya (2004e).
 ^f Chervonnyi and Chervonnaya (2005b).

electronic excited states was determined from the excitation energies of the R^+ ions, whereas the latter were obtained with the use of the thermodynamic functions in which this contribution was determined from the excitation energies of RX.

The thermodynamic functions of RX, RF_2 , and RF_3 were used in the calculations of the enthalpies of reactions. In addition, calcium and barium monofluorides, tungsten tetra- and hexafluorides, and barium monochloride are among the reaction components. Their thermodynamic functions, as well the thermodynamic functions of lanthanides in the gas phase, were taken from the database IVTANTERMO (2004).

Some data listed in Table 73 deserve comments. The data from Zmbov and Margrave (1966a,c, 1967a) were presented in the original works only in graphical form. Therefore, the K_p° magnitudes were found by computer digitization of these plots and the *A* and *B* coefficients were determined by a least-squares procedure. However, for reactions (7), (16), (18), (20), (22), and (23), the enthalpies of reaction at temperature *T* calculated from the coefficient *B* by the second law, $\Delta_r H^{\circ}(T, \text{II law})$, do not coincide with the value reported by Zmbov and Margrave (1966a,c, 1967a). This discrepancy is presumably due to the inaccuracy of the representation of semilogarithmic plots in the corresponding figures. These figures were reproduced by Zmbov and Margrave (1968) who did not give any information on correcting the results they presented earlier (Zmbov and Margrave, 1966a,c, 1967a). Therefore, the initial $\Delta_r H^{\circ}(T, \text{II law})$ values (Zmbov and Margrave, 1966a,c, 1967a) for the above reactions were used in our calculations.

The primary analysis of the data from Tables 73 and 74 allows us to suggest a scheme for calculating the enthalpies of atomization of lanthanide mono- and difluorides.

The differences in the calculated corrections for electronic excitation of RX are more pronounced for monochlorides for which the reaction of the same type is considered. It follows from Table 74 that the coinciding $\Delta_r H^{\circ}(0, \text{III law})$ and $\Delta_r H^{\circ}(0, \text{II law})$ values were obtained for the reactions involving EuCl, YbCl, and LuCl (see explanation about thermodynamic functions of these molecules in previous section). The difference between the $\Delta_r H^{\circ}(0, \text{III law})$ values from the sixth and eighth columns, within $\pm 5 \text{ kJ/mol}$, is typical of the reactions involving LaCl, CeCl, GdCl, and ErCl, whereas this difference is smaller for the other reactions. It is precisely for these compounds that the correction for electronic excitation in the calculation of the reduced Gibbs energy differs by more than $\pm 3 \text{ J/(mol·K)}$.

Comparison of the $\Delta_r H^{\circ}(0, \text{ III law})$ and $\Delta_r H^{\circ}(0, \text{ II law})$ values shows that the discrepancy between them is basically within $\pm 5 \text{ kJ/mol}$ when the correction based on the R⁺ excitation energies is introduced. Exceptions are reactions involving LaCl, CeCl, and GdCl for which the difference between the enthalpies determined by the third and second laws lies in the range 5.4–5.7 kJ/mol. The use of the thermodynamic functions in which the correction was calculated from the RCl excitation energies produces a considerably larger difference between the $\Delta_r H^{\circ}$ (0, III law) and $\Delta_r H^{\circ}(0$, III law) values. For instance, for reactions involving SmCl, GdCl, TbCl, DyCl, and ErCl, this difference is larger than ± 5 kJ/mol. For reaction (8), the difference is 23.9 kJ/mol while a somewhat smaller value (13.5 kJ/mol) is determined for reaction (9).

Applying the correction for electronic excitation leads to a more pronounced difference in the reduced Gibbs energies for monofluorides. Close (or coincident) reduced Gibbs energies were obtained for EuF, YbF, and LuF, whereas for several other RF (except NdF, PmF, and TmF), the differences are in the range 5–9 J/(mol·K). The effect of these differences on the enthalpies of reaction was considered for reactions (2), (4), (5), (10), (11), (13), (14), (17)–(19), (20), (21), (25), (28), and (29). As follows from Table 73, all the selected reactions involve monofluorides and the stoichiometric coefficients for all components are equal to unity. Another observation is the fact that for reactions with other stoichiometric coefficients, the data calculated by the second and third laws can be unreasonably scattered (see Hildenbrand, 1995).

Among the 16 pairs of $\Delta_r H^{\circ}(0, \text{ III law})$ values, the difference for 11 pairs of data is within ±4.3 kJ/mol, and this difference is larger only for reactions (2), (10), (11), (18), and (21). Analogous comparison of $\Delta_r H^{\circ}$ (0, II law) data pairs shows that the difference between the results is larger. For ten of them, the difference is on the order of ±5.6 kJ/mol, and it is even larger for the other six pairs of data. Comparison of $\Delta_r H^{\circ}$ (0, III law) and $\Delta_r H^{\circ}(0, \text{ II law})$ calculated with the same set of thermodynamic functions shows that similar to what was observed for RCl, calculations with the functions in which correction for electronic excitation is determined from the R⁺ ion excitation energies ensure a better agreement. This is especially noticeable for reactions (17)–(19).

11.2 Atomization enthalpies of RCl

Using the enthalpy of atomization of barium monochloride $\Delta_{at}H^{\circ}$ (BaCl, 0) = 440.0 kJ/mol (IVTANTERMO, 2004), we calculated the enthalpies of atomization of RCl molecules from the enthalpies of reactions (1)–(14) collected in Table 74. The results are presented in Table 75 (columns 2–5).

For comparison, the sixth column of Table 75 contains the enthalpies of atomization $\Delta_{at}H^{\circ}(0, \text{ EI})$ of RCl found from measurements of the R⁺ appearance energies during ionization of these molecules by electron impact (Sapegin, 1984) with the use of the IE(R) values from the NIST Ground Levels database. Since thermodynamic functions were not used

R	$\Delta_{at} \mathcal{H}^{\circ}$ (0, III law) ^a	$\Delta_{at} \mathcal{H}^{\circ}(0, II \ law)^{a}$	$\Delta_{at} \mathcal{H}^{\circ}$ (0, III law) b	$\Delta_{at} \mathcal{H}^{\circ}$ (0, II law) ^b	$\Delta_{at} \mathcal{H}^{\circ} (0, El)^{c}$	$\Delta_{at} \mathcal{H}^{\circ}(0)^{d}$
1	2	3	4	5	6	7
La	500.1 ± 0.4	505.5 ± 7.9	506.9 ± 0.4	509.0 ± 0.4	501.0 ± 7.7	521.6
Ce	490.1 ± 0.4	495.8 ± 6.0	495.9 ± 0.4	496.7 ± 0.4	(498)	457.0
Pr	470.2 ± 0.4	471.3 ± 3.6	472.0 ± 0.4	476.1 ± 0.4	462.7 ± 7.7	423.5
Nd	448.2 ± 0.4	448.6 ± 2.2	448.8 ± 0.4	451.8 ± 0.4	443.3 ± 6.8	418.7
Pm	(436)	-	(436)	-	(430)	413.9
Sm	431.4 ± 0.2	428.4 ± 1.7	435.0 ± 0.2	427.1 ± 1.7	423.2 ± 5.8	418.7
Eu	419.1 ± 0.6	416.2 ± 9.2	419.1 ± 0.6	416.2 ± 9.2	404.2 ± 5.8	405.5
Gd	466.9 ± 0.7	472.5 ± 4.4	477.7 ± 0.7	469.8 ± 4.4	475.6 ± 6.8	451.0
Tb	457.1 ± 0.4	460.0 ± 2.8	461.5 ± 0.4	485.4 ± 2.8	(465)	470.1
Dy	411.7 ± 1.1	411.5 ± 5.5	409.5 ± 1.1	423.0 ± 5.5	411.1 ± 5.8	392.4
Ho	418.4 ± 0.5	419.4 ± 2.6	422.9 ± 0.5	424.6 ± 2.6	416.6 ± 7.7	409.1
Er	429.1 ± 0.4	429.1 ± 2.2	434.4 ± 0.4	429.0 ± 2.2	(436)	448.6
Tm	383.7 ± 1.1	382.2 ± 8.6	383.2 ± 1.1	387.7 ± 8.6	392.3 ± 5.8	378.0
Yb	361.2 ± 0.2	361.5 ± 1.6	361.2 ± 0.2	361.5 ± 1.6	368.2 ± 5.8	374.4
Lu	461.9 ± 0.4	462.2 ± 2.3	461.9 ± 0.4	462.2 ± 2.3	(460)	380.4

TABLE 75 Enthalpies of atomization of lanthanide monochlorides (kJ/mol)

^{*a*} Calculated using the thermodynamic functions in which the electronic component was determined from the excitation energies of R⁺ ions. ^{*b*} Calculated using the thermodynamic functions in which the electronic component was determined from the excitation energies of RCI.

^c Calculated from the appearance energies of R⁺ ions during ionization of RCl molecules by electron impact (Sapegin, 1984) with the use of the R ionization energies from NIST Ground Levels.

^d Reported by Kaledin et al. (1999). Estimated values are given within parentheses: our data for PmCl and the data from Sapegin (1984) for CeCl, PmCl, TbCl, ErCl, and LuCl.

for calculating these $\Delta_{at}H^{\circ}(0, \text{ EI})$ values, their comparison with the data in columns 2–5 in Table 75 allows one to judge the quality of the thermodynamic functions of RCl.

The use of thermodynamic functions corrected for the electronic excitation of RCl determined from the excitation energy of the free R^+ ion leads to smaller deviations from the experimental data (Sapegin, 1984) not only in calculations according to the third law but also for those made according to the second law.

The seventh column in Table 75 contains the data from Kaledin et al. (1999), which were found, like the electronic excitation energies of RX, with the use of the LFT. As is seen, these data differ considerably from the set of experimental data.

Taking into account the above arguments in favor of the use of the excitation energies of the free R^+ ion in calculations of the correction to thermodynamic functions for electronic excitation of RX, we deem it more appropriate to calculate the standard enthalpies of atomization of RF and RF₂ from the enthalpies of reaction presented in the sixth and seventh columns of Table 73 and, then, to use the data from the eighth and ninth columns in the same calculations for comparison.

11.3 Scheme of calculation of standard atomization enthalpies of RF and RF_2

In general, the standard enthalpy of a gas-phase chemical reaction

$$v_1A_1 + v_2A_2 + \dots = v'_1A'_1 + v'_2A'_2 + \dots$$

can be calculated from the standard enthalpies of atomization of its components by the equation

$$\Delta_{\mathbf{r}}H^{\circ}(0) = v_{1}\Delta_{\mathrm{at}}H^{\circ}(A_{1},0) + v_{2}\Delta_{\mathrm{at}}H^{\circ}(A_{2},0) + \dots - v'_{1}\Delta_{\mathrm{at}}H^{\circ}(A'_{1},0) - v'_{2}\Delta_{\mathrm{at}}H^{\circ}(A'_{2},0) - \dots$$
(36)

Thus, it is evident that $\Delta_{at}H^{\circ}(0)$ for one component of the reaction can be calculated if analogous data are available for the other components. It is easy to recognize that, among the reactions involving RF_x molecules (x = 1, 2, 3), there are many from which the enthalpy of atomization of a given component can be calculated using the $\Delta_{at}H^{\circ}(0)$ values for the other components from reliable data sources (hereinafter, such components are referred to as references). However, there are some reactions for which $\Delta_{at}H^{\circ}(0)$ values are unknown for one or more components. In such cases, the $\Delta_{at}H^{\circ}(0)$ values preliminarily found in the other reactions under consideration should be used as references in calculations. Based on this criterion, we classified the reactions studied into five groups. The first group comprises reactions (7) and (27), which do not involve lanthanide mono and/or difluorides. Henceforth, the calculations for these reactions only allow one to judge the quality of measurements of the equilibrium constants (Zmbov and Margrave, 1966a,c). Indeed, the use of $\Delta_{at}H^{\circ}(NdF_3, 0) = 1792$. 2 kJ/mol and the $\Delta_rH^{\circ}(0, \text{III law})$ and $\Delta_rH^{\circ}(0, \text{III law})$ values for reaction (7) from Table 73 gives $\Delta_{at}H^{\circ}(BaF, 0) = 570.5$ and 532.6 kJ/mol, respectively. Comparison of these values with the recommended one (580.0 kJ/mol) (see IVTANTERMO, 2004) allows us to regard the third law calculations as satisfactory.

The enthalpy of reaction (27) ($\Delta_r H^\circ(0, \text{III law}) = -22.4 \pm 0.9 \text{ kJ/mol}$ and ($\Delta_r H^\circ(0, \text{III law}) = -21.5 \pm 6.7 \text{ kJ/mol}$) is the difference between the enthalpies of atomization of HoF₃ and ErF₃. The difference derived from the standard thermodynamic parameters of RF₃ calculated from experimental saturated vapor pressures is -10.2 kJ/mol ($\Delta_{at}H^\circ$ (HoF₃, 0) = 1769.7 kJ/mol and $\Delta_{at}H^\circ(\text{ErF}_3, 0) = 1$ 779. 9 kJ/mol). In this case, calculations according to both the second and third laws lead to a discrepancy of ~10 kJ/mol.

The second group includes the reactions in which $\Delta_{at}H^{\circ}(0)$ is determined only through the enthalpy of reaction and the enthalpy of atomization found in independent studies. This group comprises reactions involving CaF, BaF, RF₃, WF₄, and WF₅. The corresponding enthalpies of atomization were taken from IVTANTERMO (2004) and Chervonnyi and Chervonnaya (2007a).

The third group corresponds to reactions (1) and (2) involving lanthanum fluorides. There are two such reactions and two unknown enthalpies of atomization, $\Delta_{at}H^{\circ}(LaF_2, 0)$ and $\Delta_{at}H^{\circ}(LaF, 0)$. Thus, taking into account the known $\Delta_{at}H^{\circ}(BaF, 0)$ value, both unknown values can be determined from the enthalpies of reactions (1) and (2), $\Delta_r H^{\circ}(1, 0)$ and $\Delta_r H^{\circ}(2, 0)$ (see Eqs. (34) and (35)). To do this, we first calculated the enthalpy of atomization for LaF₂ and then for LaF.

The fourth group includes reactions (5), (11), (12), (14), (29), and (30) involving monofluorides whose enthalpies of atomization are determined in the reactions of the second group.

The fifth group comprises reactions in which one component is holmium monofluoride. The reliability of determination of $\Delta_{at}H^{\circ}(HoF, 0)$ ensures the reliability of calculation of the enthalpies of atomization of GdF, GdF₂, DyF, HoF₂, ErF, and ErF₂.

The enthalpies of atomization of RF and RF_2 calculated from the thermodynamic functions corrected for RF electronic excitation based on the R^+ excitation energies are summarized in Table 76.

The first column in Table 76 specifies a 4f element for which $\Delta_{at}H^{\circ}$ (RF, 0) or $\Delta_{at}H^{\circ}$ (RF₂, 0) is calculated from some reaction. This makes it possible to clearly elucidate the order of the distribution of reactions to

			$\Delta_{at}H^{\circ}(RF,O) \qquad \Delta_{at}H^{\circ}(RF_{2},O)$		₂ , 0))		Recommended values	
R	Reaction	No.		II	III	II	Reference ^a	$\Delta_{ t at} {m H}^{\circ}$ (RF, 0)	$\Delta_{at}H^{\circ}$ (RF ₂ , 0)
1	2	3	4 ^b	5 ^b	6 ^b	7 ^b	8	9	10
La	$La + LaF_2 = 2LaF$	(1)	627.9	673.6	_	_	_	643.9	1272.1
	$Ba + LaF_2 = BaF + LaF$	(2)	-	-	1271.3	1328.5	_	-	-
	LaF + Ba = BaF + La	(3)	631.7	-	-	-	BaF (580.0)	-	-
Ce	_	_	-	-	-	-	_	(626)	(1250)
Pr	_	_	-	-	-	-	_	(604)	(1214)
Nd	Ba + NdF = BaF + Nd	(4)	579.6	574.3	-	-	BaF (580.0)	579.6	1175.6
	$Ba + NdF_2 = BaF + NdF$	(5)	-	-	1175.6	1186.9	NdF (579.6), BaF (580.0)	-	-
	$2BaF + Nd = 2Ba + NdF_2$	(6)	_	_	1174.1	1178.1	BaF (580.0)	-	_
	$NdF_3 + 2Nd = 3NdF$	(8)	567.7	548.1	-	-	NdF ₃ (1792.207)	-	-
	$2NdF_3 + Nd = 3NdF_2$	(9)	-		1145.2	1133.2	NdF ₃ (1792.207)	-	-
Pm	_	_	_	_	_	_		(566)	(1170)
Sm	Sm + CaF = SmF + Ca	(10)	555.7	566.9	_	_	CaF (530.0)	555.7	(1160)
	$SmF + CaF = SmF_2 + Ca$	(11)	_		1110.5	1118.1	SmF (555.7), CaF (530.0)	-	_

TABLE 76 Enthalpies of atomization of lanthanide mono- and difluorides (kJ/mol)

(continued)

TABLE 76 (continued)

			$\Delta_{ m at} {m H}^{\circ}({ m RF},{ m 0})$		$\Delta_{at} \mathcal{H}^{\circ}(RF_2,0)$			Recomm values	ΔatH° (RF ₂ , 0) 10 - (1143) - 1213.5
R	Reaction	No.	III	II		11	Reference ^a	$\Delta_{ t at} {m H}^{\circ}$ (RF, 0)	$\Delta_{ m at} H^{\circ}$ (RF ₂ , 0)
1	2	3	4 ^b	5 ⁶	6 ^b	7 ⁶	8	Recommended values $\Delta_{at}H^{\circ}$ $\Delta_{at}H^{\circ}$ $\Delta_{at}H^{\circ}$ $\Delta_{at}H^{\circ}$ $\Delta_{at}H^{\circ}$ $\Delta_{at}H^{\circ}$ $\overline{9}$ $\overline{10}$ 555.7), $ \overline{9}$ $\overline{10}$ 555.7), $ \overline{9}$ $\overline{10}$ 555.7), $ \overline{3}$ $\overline{9}$ $\overline{30.0}$ 549.5 $\overline{30.0}$ 549.5 $\overline{30.0}$ $\overline{549.5}$ $\overline{2085.2}$, $ \overline{530.0}$ $\overline{57.5}$, $\overline{3}_3$ $\overline{57.5}$, $\overline{57.5}$, $ \overline{3}_3$ $\overline{7.4}$ $\overline{557.5}$, $ \overline{3}_2$ $\overline{57.5}$, $\overline{42.22}$, $\overline{7.614.6}$ $\overline{557.5}$, $ \overline{3}_2$ $\overline{57.5}$, $\overline{57.5}$, $-$	10
	$SmF + SmF_3 = 2SmF_2$	(12)	_		1124.5	1120.0	SmF (555.7), SmF ₃ (1699.4)	_	-
Eu	Eu + CaF = EuF + Ca	(13)	541.5	545.6	_	_	CaF (530.0)	549.5	(1143)
	Eu + CaF = EuF + Ca	(13)	545.1	549.5	_	_	CaF (530.0)		. ,
	$EuF + CaF = EuF_2 + Ca$	(14)	-	-	1089.4	1092.3	EuF (549.5), CaF (530.0)	-	-
	$EuF_3 + WF_4 = EuF_2 + WF_5$	(15)	-	-	1174.0	1126.9	WF ₄ (2085.2), WF ₅ (2524.3), EuF ₃ (1633.9)	-	-
Gd	$2\text{HoF} + \text{GdF} = 2\text{Ho} + \text{GdF}_3$	(16)	626.6	614.6	-	-	HoF (557.5), GdF ₃ (1867.4)	614.6	1213.5
	$GdF + HoF_2 = GdF_2 + HoF$	(17)	-	-	1213.5	1225.8	HoF (557.5), HoF ₂ (1142.2), GdF (614.6)		-
	$GdF_2 + HoF = GdF_3 + Ho$	(18)	-	-	1224.7	1219.2	HoF (557.5), GdF ₃ (1867.4)	_	-

Tb	_	_	-	-	-	-	-	(604)	(1192)
Dy	Ho + DyF = HoF + Dy	(19)	546.5	546.5	-	-	HoF (557.5)	546.5	(1130)
Ho	Ho + SmF = HoF + Sm	(20)	557.5	545.3	-	-	SmF (555.7)	557.5	1142.2
	Ho + EuF = HoF + Eu	(21)	536.6	563.5	-	-	EuF (549.5)		_
	$3HoF = 2Ho + HoF_3$	(22)	553.8	557.7	-	-	HoF ₃ (1769.7)		_
	$HoF_2 + Ho = 2HoF$	(23)	_	_	1142.2	1130.0	HoF (557.5)	-	-
	$3\text{HoF}_2 = 2\text{HoF}_3 + \text{Ho}$	(24)	-	_	1133.8	1152.3	HoF ₃ (1769.7)	-	_
Er	HoF + Er = Ho + ErF	(25)	574.0	581.9	-		HoF (557.5)	574.0	1158.3
	$HoF_2 + Er = Ho + ErF_2$	(26)	-	_	1158.3	1162.7	HoF ₂ (1142.2)	-	_
Tm	Tm + CaF = TmF + Ca	(28)	514.5	509.3	-	-	CaF (530.0)	514.5	1095.5
	$TmF + CaF = TmF_2 + Ca$	(29)	-	-	1095.5	1074.9	TmF (514.5), CaF (530.0)	-	-
	$TmF + TmF_3 = 2TmF_2$	(30)	-	-	1091.8	1078.4	TmF (514.5), TmF ₃ (1703.8)	-	_
Yb	_	_	_	_	_	_	_	(486)	(1075)
Lu	_	_	_	_	_	_	-	(623)	(1206)

^a The enthalpy of atomization assigned to a given compound is given in parentheses.
 ^b The enthalpies of atomization calculated from the enthalpies of reaction determined by the third law are given in the fourth and sixth columns; analogous data calculated from the enthalpies of reaction determined by the second law are listed in the fifth and seventh columns.

ensure roughly the same possibilities in calculation of $\Delta_{at}H^{o}(0)$. We succeeded in calculating this characteristic parameter for nine monofluorides and eight difluorides.

We believe that the calculation of the enthalpies of atomization of samarium and europium fluorides from the data reported by Kleinschmidt et al. (1981) is more correct and that the reactions involving SmF and EuF studied by Zmbov and Margrave (1967a) should be considered when discussing $\Delta_{at}H^{\circ}$ (HoF, 0). In addition, we tried to calculate both $\Delta_{at}H^{\circ}$ (RF, 0) and $\Delta_{at}H^{\circ}$ (RF₂, 0) from the enthalpies of reactions with low stoichiometric coefficients.

11.4 Choice of recommended $\Delta_{at}H^{\circ}(RF, 0)$ values

As follows from Table 76, that for some monofluorides, the enthalpies of atomization were calculated with the use of the $\Delta_r H^{\circ}(0, \text{ III law})$ and $\Delta_r H^{\circ}(0, \text{ III law})$ values measured in two different reactions. This is not the case for GdF and for HoF; such calculations were based on measurements on three reactions. In this context, it is necessary to choose the most reliable value among them. This problem was solved in three steps.

The enthalpy of atomization of HoF was selected first. In addition to the values obtained by processing the data for reactions (20)–(22), we obtained information from the calculations of some heterogeneous equilibria studied by Zmbov and Margrave (1966c, 1967a) who reported relative equilibrium constants for four reactions (Table 77). The absence of absolute K_p° values made it possible to calculate the enthalpies of these reactions only by the second law and, then, to determine the enthalpy of atomization of BaF, SmF, EuF, and HoF using the $H^{\circ}(T)$ - $H^{\circ}(0)$ enthalpies for neodymium, samarium, europium, barium, and barium-containing compounds from the database IVTANTERMO (2004) and for RF(g) and RF₃(cr, liq) from Chervonnyi and Chervonnaya (2007a,d).

Comparison of these results with the corresponding data in Table 76 shows that all of them are underestimated. The same is observed for $\Delta_{at}H^{\circ}$ (BaF, 0), as follows from comparison with the analogous characteristic parameters in IVTANTERMO (2004). It is worth noting that the best agreement with the experimental results of gas-phase equilibria was obtained for HoF. Nevertheless, taking into account the same origin for the systematic error in the final values listed in Table 77, we chose the value 557.5 kJ/mol, which was obtained not only by the third law with data from reaction (20) but also by the second law with data from reaction (22). The results for reaction (21) should be declared invalid because they lead to a large discrepancy between the $\Delta_{at}H^{\circ}(0, \text{II law})$ and $\Delta_{at}H^{\circ}$ (0, III law) values for holmium monofluoride. As follows from the data in the eighth column of Table 76, the value 557.5 kJ/mol was used for

Reaction	No.	Т (К)	∆ _r H°(T, II law) 4	∆ _r H°(0, II law) ^e	∆ _{at} H°(MF, 0, II law) ^a	∆ _r H°(0, II law) ^b	∆ _{at} H°(MF, 0, II law) ^b	References
1	2	3	4	5	6	7	8	9
$\frac{2\text{BaF}(g) = \text{Ba}(g) + }{\text{BaF}_2(s)}$	(1)	1514– 1365	-382.8 ± 15.1	-435.3 ± 15.1	554.8	$\begin{array}{r}-435.3\pm\\15.1\end{array}$	554.8	С
3NdF(g) = 2Nd(g) + $NdF_3(s)$	(2)	1412– 1510	-529.7 ± 21.3	-565.1 ± 21.3	557.3	-545.3 ± 21.3	563.9	С
$3SmF(g) = 2Sm(g) + SmF_3(s)$	(3)	1151– 1241	-558.1 ± 12.6	$\begin{array}{c}-586.8\pm\\12.6\end{array}$	515.4	-596.3 ± 12.6	512.2	d
3EuF(g) = 2Eu(g) + $EuF_3(s)$	(4)	1265– 1423	-483.7 ± 12.6	$\begin{array}{r}-534.4\pm\\12.6\end{array}$	495.1	-533.9 ± 12.6	495.2	d
3HoF(g) = 2Ho(g) + $HoF_3(s)$	(5)	1238– 1401	$\begin{array}{r}-533.9\pm\\8.4\end{array}$	$\begin{array}{c}-568.4\pm\\8.4\end{array}$	553.4	$\begin{array}{r}-555.4\pm\\8.4\end{array}$	557.7	е
3HoF(g) = 2Ho(g) + HoF ₃ (s)	(6)	1317– 1424	$\begin{array}{c} -528.0 \pm \\ 8.4 \end{array}$	$\begin{array}{r}-563.8\pm\\8.4\end{array}$	554.9	$\begin{array}{c}-550.2\pm\\8.4\end{array}$	559.4	d

TABLE 77 Enthalpies of some heterogeneous reactions and enthalpies of atomization of monofluorides involved in these reactions

^{*a*} Calculated using the thermodynamic functions in which the electronic component was determined from the excitation energies of R^+ ions. ^{*b*} Calculated using the thermodynamic functions in which the electronic component was determined from the excitation energies of RF. Here, $\Delta_{at}H^{\circ}$ (MF, 0, II law) is the enthalpy of atomization of MF (M = Ba, Nd, Sm, Eu, and Ho) calculated from the enthalpy of the corresponding reaction determined by the second law.

^c Zmbov and Margrave (1966a).
 ^d Zmbov and Margrave (1967a).
 ^e Zmbov and Margrave (1966c).

determining the enthalpies of atomization from the experimental data for the reactions of the fifth group.

The second step involves analysis of the ratio $\Delta_{at}H^{\circ}(RF, 0)/\Delta_{at}H^{\circ}(RCl, 0)$ as a function of the atomic number of the 4f element (n = 1-15 for R = La-Lu). For all RF, except LaF, the $\Delta_{at}H^{\circ}(RF, 0)$ values were taken from the fourth and fifth columns of Table 76. The corresponding values for RCl were taken from the second column of Table 75. For LaF and LaCl, the thermodynamic functions are known (Chervonnyi and Chervonnaya, 2007e) for which the correction for electronic excitation was calculated from the experimental electronic excitation energies of these molecules. Therefore, we deemed it more correct to calculate the $\Delta_{at}H^{\circ}(LaF, 0)/\Delta_{at}H^{\circ}$ (LaCl, 0) ratio from the values found by Chervonnyi and Chervonnaya (2007e) on the basis of these functions.

We found (Figure 45) that many of these ratios are described with a high degree of accuracy by the polynomial

$$\frac{\Delta_{\rm at}H^{\circ}(\rm RF,0)}{\Delta_{\rm at}H^{\circ}(\rm RCl,0)} = 1.26276 + 0.00798n - 1.49133 \times 10^{-4}n^2, \qquad (37)$$

where n = 1-15 for R = La-Lu.



FIGURE 45 $\Delta_{at}H^{\circ}(RF, 0)/\Delta_{at}H^{\circ}(RCl, 0)$ versus n (n = 1-15 for R = La-Lu). The electronic contribution to the thermodynamic functions of RF was determined from the excitation energies of free R^+ ions (R = Ce-Lu). Solid line, approximating polynomial; \Box , values obtained from $\Delta_{at}H^{\circ}(0, III law)$; and \blacktriangle , data obtained from $\Delta_{at}H^{\circ}(0, III law)$. Reproduced from Chervonnyi and Chervonnaya (2007f) with permission from Pleiades Publishing, Ltd.

The polynomial was constructed with the help of 10 of the 27 ratios for 8 of the 9 monofluorides studied (SmF being set aside). Among the $\Delta_{at}H^{\circ}$ (RF, 0) values used for elaborating the polynomial, six values were calculated by the third law and four values were obtained by the second law. For DyF and HoF, both variants of calculation of the enthalpy of atomization (by the second and third laws) were included. For two monofluorides (EuF and GdF), the enthalpies of atomization calculated from $\Delta_r H^{\circ}(0, \text{ II law})$ were used. In this context, the following comments are pertinent.

As follows from Table 73, two series of measurements of the equilibrium constant were performed for reaction (13) in temperature ranges with a difference of ~100 K between the corresponding upper and lower limits. This originated from the conditions used for the experimental measurements. In the case of the low-temperature range experiment, calcium and europium monofluorides were synthesized by reacting $CaF_2(g)$ and $EuF_3(g)$ with solid boron. In the high-temperature range, the same monofluorides were synthesized by the reaction of $CaF_2(g)$ with Eu_2O_3 (solid). The latter procedure is preferred.

Measurement of the equilibrium constants of the gas-phase reactions in a Gd-HoF₃ mixture at high temperatures faced some difficulties (Zmbov and Margrave, 1967a). In the range 1358–1514 K, only the R⁺, RF^+ , and RF_2^+ ions were detected. The use of ionizing electron energies 5 eV higher than the corresponding ionization threshold led to unreliable detection of Gd⁺ ions, which formed in the course of ionization of atomic gadolinium. In addition, due to the lack of the GdF_3^+ ion in the mass spectrum, the ion current proportional to the GdF₃ partial pressure was determined from the intensity of the GdF_2^+ ion at an energy of 18 eV (Zmbov and Margrave, 1967a). As was shown by these authors, at this energy, the GdF_2^+ ion is generated not only from GdF_2 (ionization threshold, 6.5 ± 0.3 eV) but also from GdF₃ (appearance energy, 12.2 ± 0.5 eV). However, the procedure of decomposition of the ion current intensity into two components is the source of additional errors on the determination of K_{p}° . On the other hand, the effect of this factor on the temperature dependence of the equilibrium constant (and on the subsequent second-law calculation of the enthalpy of reaction) is insignificant. Therefore, the enthalpies of atomization derived from the enthalpies of reaction calculated by the third law can hardly be reliable. In this case, the values calculated by the second law are more dependable.

The final step involves the determination of the enthalpies of atomization of CeF, PrF, PmF, TbF, YbF, and LuF with the use of polynomial (37) and the corresponding $\Delta_{at}H^{\circ}(RCl, 0)$ values from the second column of Table 75. The resulting series of $\Delta_{at}H^{\circ}(RF, 0)$ values is listed in the ninth column of Table 76.

11.5 Choice of recommended $\Delta_{at}H^{\circ}(RF_2, 0)$ values

To estimate the results of processing the experimental data and choose the most reliable $\Delta_{at}H^{\circ}(RF_2, 0)$ values, we compared these values with analogous characteristic parameters of lanthanide dichlorides. The series of RCl₂ compounds has been comprehensively studied. Parameters obtained by independent methods (electron-impact method, study of gas-phase equilibria, study of thermodynamics of evaporation and sublimation) are available. Detailed analysis of these experimental data has been described by Chervonnyi and Chervonnaya (2008b). As a result, standard enthalpies of atomization were obtained for the entire 4f series. Therefore, the $\Delta_{at}H^{\circ}(RCl_2, 0)$ values determined these authors are used in the procedure described below.

As in the case of RX, we considered the ratio $\Delta_{at}H^{\circ}(RF_2, 0)/\Delta_{at}H^{\circ}(RCl_2, 0)$ as a function of the atomic number of the 4f elements. Although the scatter of these values is rather large, half of them can be approximated by a straight line: these values show a weak tendency to decrease in going from lanthanum to lutetium.

The scatter of the $\Delta_{at}H^{\circ}(RF_2, 0)$ values that can be used in the approximation procedure was calculated to be within $\pm 10 \text{ kJ/mol}$. According to our estimates, this range corresponds to the assumed error of determination of the enthalpy of atomization of RF_2 by the method used. It is worth noting that analogous estimates performed for the selected ratios used in approximating polynomial (37) lie in the range $\pm 1.2 \text{ kJ/mol}$.

It is easy to see that the enthalpies of atomization of six difluorides (except SmF_2 and EuF_2) fit in the above relationship. LaF_2 is represented by one value found by the third law; NdF_2 and GdF_2 are represented by four values each (two values calculated by the third law and two values found by the second law); and HoF₂, ErF_2 , and TmF_2 are represented by two values each. The first two difluorides have one value calculated by the second law and one value calculated by the third law. For TmF_2 , both values were determined by the third law. In this context, we believe that the set of the available data is representative and applicable to the estimation of the enthalpies of atomization for the entire RF_2 series.

Approximation of selected ratios led to the following analytical expression that relates these ratios to the atomic number of a 4f element *n*:

$$\frac{\Delta_{\rm at}H^{\circ}(\rm RF_2,0)}{\Delta_{\rm at}H^{\circ}(\rm RCl_2,0)} = 1.28114 - 5.5574 \times 10^{-4}n. \tag{38}$$

Using this expression and the $\Delta_{at}H^{\circ}(RCl_2, 0)$ values from Chervonnyi and Chervonnaya (2008b), we calculated the enthalpies of atomization of all difluorides and compared them with the corresponding values from the sixth and seventh columns of Table 76. The exception is the $\Delta_{at}H^{\circ}$ (LaF₂, 0) value, which was calculated from the thermodynamic functions of LaF corrected for the electronic excitation of this molecule. Among the values thus selected, the 10th column of Table **76** contains the values calculated by the third law for six difluorides: LaF₂, NdF₂, GdF₂, HoF₂, ErF₂, and TmF₂. For the rest of the compounds considered, the 10th column of Table **76** gives the estimates of $\Delta_{\rm at}H^{\circ}(\rm RF_2, 0)$.

In our opinion, the discrepancies revealed between the estimates and the $\Delta_{at}H^{\circ}(RF_2, 0)$ values obtained by processing experimental data (Kleinschmidt et al., 1981) require further discussion. Indeed, according to Table 76, measurements of the equilibrium constants for the reactions

$$R + CaF = RF + Ca$$
 ($R = Sm, Eu, Tm$)

led not only to good results from the standpoint of the consistency of the enthalpies of atomization obtained by the second and third laws but also, eventually, to their recommended values.

At the same time, the enthalpies of atomization of corresponding difluorides determined from the experimental data for the reaction

$$RF + CaF = RF_2 + Ca (R = Sm, Eu)$$

or

$$SmF + SmF_3 = 2SmF_2$$

are considerably lower than the recommended values, although the difference between the enthalpies of atomization found by the second and third laws is small. Opposite trends are observed for similar reactions involving thulium fluorides. The $\Delta_{at}H^{\circ}$ (TmF₂, 0) values obtained for reactions (29) and (30) by the third law are close to each other, one of them being recommended; however, the second-law calculations lead to noticeably underestimated values.

If we consider reactions (10) and (11), assuming that the Ca⁺, CaF⁺, and SmF⁺ ion currents in reaction (10) have been measured rather accurately, we can draw the conclusion that the SmF₂⁺ ion current measured in reaction (11) is in error by about two orders of magnitude. This can be a source of difference (~50 kJ/mol) between the enthalpies of atomization of SmF₂ listed in the 6th and 10th columns of Table 76. It is difficult to detect which factor is responsible for such a large difference. However, some conclusions about the quality of these measurements can be drawn from analysis of temperature dependences of equilibrium constants.

For reaction (11), 20 K_p° values measured in the range 1448–1643 K were reported by Kleinschmidt et al. (1981). The plot of lg K_p° versus 10³/ *T* shows a relatively wide scatter of data. The enthalpy of reaction $\Delta_r H^\circ$ (0, II law) derived from these data is -32.4 ± 5.9 kJ/mol (Table 73). However, for 10 of the 20 experimental data points in the range 1480–1564 K, the same calculation gives $\Delta_r H^\circ$ (0, II law) = -70.6 ± 10.5 kJ/mol.

This value leads to $\Delta_{at}H^{\circ}(SmF_2, 0) = 1156.3 \text{ kJ/mol}$, which is consistent with our estimates.

Another similar example is $\Delta_{at}H^{\circ}(\text{TmF}_{2}, 0) = 1074.9 \text{ kJ/mol}$ obtained by second-law calculations from the $\Delta_{r}H^{\circ}(T, \text{ II law})$ value for reaction (29), which was found by Kleinschmidt et al. (1981) by joint processing K_{p}° measurements in two temperature ranges, 1447–1564 K and 1797–1926 K. However, separate calculations for the first and second temperature ranges give -7.9 and -50.2 kJ/mol, respectively. The second value nearly coincides with $\Delta_{r}H^{\circ}(0, \text{ III law})$ for the same reaction.

Kleinschmidt et al. (1981) were likely aware of the low quality of measurements of equilibrium constants in some cases and tried to obtain additional data in order to remove doubts. In particular, they measured the equilibrium constants of reaction (15) involving tungsten tetra- and pentafluorides, whose thermodynamic properties were preliminarily studied in the same laboratory (Hildenbrand, 1975). As follows from Table 76, our processing of the measurements for this reaction affords $\Delta_{at}H^{\circ}(EuF_2, 0)$ values either higher (third-law calculations) or lower (second-law calculations) than the estimated value. In our opinion, the measurements of K_{p}° of reaction (15) are more reliable. A reason for this conclusion is the value $\Delta_{at}H^{\circ}(\text{EuF}_{2}, 0) = 1633.9 \text{ kJ/mol}$ (see Chervonnyi and Chervonnaya, 2007a), which we calculated by the second law from the only available measurement of the enthalpy of sublimation of europium trifluoride (Zmbov and Margrave, 1968). This value is somewhat overestimated as compared to similar data for RCl₃ (Chervonnyi and Chervonnaya, 2007g). More precise measurements of $\Delta_{sub}H^{\circ}(EuF_3, 0)$ will provide better agreement between the $\Delta_{at}H^{\circ}(EuF_3, 0)$ estimate and the value obtained from the experimental data on reaction (15).

11.6 Influence of thermodynamic functions for RF on atomization enthalpies of RF_x

The above procedure of calculation and estimation of $\Delta_{at}H^{\circ}(LaF, 0)$ and $\Delta_{at}H^{\circ}(LaF_2, 0)$ was applied to the standard enthalpies of reaction obtained with the use of the set of thermodynamic functions in which correction for electronic excitation was calculated from the excitation energies of RX. Data from the eighth and ninth columns of Table 73 were used. Correspondingly, the $\Delta_{at}H^{\circ}(LaCl, 0)$ values from the eighth column of Table 74 were used for calculating the $\Delta_{at}H^{\circ}(LaF, 0)/\Delta_{at}H^{\circ}(LaCl, 0)$ ratios. The results of these calculations are listed in Table 78.

Figure 46 shows the plots of $\Delta_{at}H^{\circ}(RF, 0)/\Delta_{at}H^{\circ}(RCl, 0)$ versus the atomic number (*n*) of a 4f element and allows us to conveniently compare the differences caused by the substitution of one set of thermodynamic functions of RX for the other.

			$\Delta_{at}H^{\circ}(RF, 0)$ $\Delta_{at}H^{\circ}(RF, 0)$			$_{at}H^{\circ}(RF_{2}, 0)$			Recommended values	
R	Reaction	No.		II		II	References ^a	$\Delta_{at} \mathcal{H}^{\circ}$ (RF, 0)	$\Delta_{at} H^\circ$ (RF ₂ , 0)	
1	2	3	4 ^{<i>b</i>}	5 ⁶	6 ^b	7 ⁶	8	9	10	
La	$La + LaF_2 = 2LaF$	(1)	643.9	679.4	_	_	_	643.9	1272.1	
	$Ba + LaF_2 = BaF + LaF$	(2)	-	-	1272.1	1328.7	-	-	-	
	LaF + Ba = BaF + La	(3)	646.9	-	-	-	BaF (580.0)	-	-	
Ce	-	_	-	_	_	_	_	(634)	(1249)	
Pr	-	_	-	_	_	_	-	(606)	(1214)	
Nd	Ba + NdF = BaF + Nd	(4)	580.0	580.6	_	_	BaF (580.0)	580.0	1175.5	
	$Ba + NdF_2 = BaF + NdF$	(5)	-	-	1175.5	1181.2	NdF (580.0), BaF (580.0)	-	-	
	$2BaF + Nd = 2Ba + NdF_2$	(6)	-	_	1174.1	1178.1	BaF (580.0)	_	-	
	$NdF_3 + 2Nd = 3NdF$	(8)	567.7	554.6	-	-	NdF ₃ (1792.2)	-	-	
	$2NdF_3 + Nd = 3NdF_2$	(9)	-		1145.2	1133.3	NdF ₃ (1792.2)	_	-	
Pm	-	_	-	_	_	_	-	(566)	(1169)	
Sm	Sm + CaF = SmF + Ca	(10)	567.1	563.6	-	-	CaF (530.0)	567.1	(1159)	
	$SmF + CaF = SmF_2 + Ca$	(11)	-		1113.3	1133.0	SmF (567.1), CaF (530.0)	-	_	
	$SmF + SmF_3 = 2SmF_2$	(12)	_		1125.8	1127.4	SmF (567.1), SmF ₃ (1699.4)	_	-	

TABLE 78 Enthalpies of atomization of lanthanide mono- and difluorides (kJ/mol)

(continued)

T,	AB	LE	78	(continued))
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			$\Delta_{ t at} {m H}^{\circ}({ t RF},{ t 0})$		$\Delta_{at} H^{\circ}(RF_2, 0)$			Recommended values	
R	Reaction	No.		11	III	11	References ^a	$\overline{\Delta_{\mathtt{at}}} \mathcal{H}^{\circ}$ (RF, 0)	$\Delta_{ t at} H^{\circ}$ (RF ₂ , 0)
1	2	3	4 ^b	5 ^b	6 ^b	7 ⁶	8	9	10
Eu	Eu + CaF = EuF + Ca Eu + CaF = EuF + Ca	(13) (13)	541.0 544.5	545.6 549.4	_	-	CaF (530.0) CaF (530.0)	549.4 _	(1142)
	$EuF + CaF = EuF_2 + Ca$	(14)	_	_	1089.9	1092.9	EuF (549.4), CaF (530.0)	-	_
	$EuF_3 + WF_4 = EuF_2 + WF_5$	(15)	_	_	1174.0	1126.9	WF ₄ (2085.2), WF ₅ (2524.3), EuF ₃ (1633.9)	-	_
Gd	$2\text{HoF} + \text{GdF} = 2\text{Ho} + \text{GdF}_3$	(16)	640.4	601.2	-	-	HoF (566.4), GdF ₃ (1867.4)	(630)	(1214)
	$GdF + HoF_2 = GdF_2 + HoF$	(17)	-	-	1187.5	1212.0	HoF (566.4), HoF ₂ (1141.0), GdF (601.2)		_
	$GdF_2 + HoF = GdF_3 + Ho$	(18)	_	_	1225.5	1214.9	HoF (566.4), GdF ₃ (1867.4)	-	_

Tb	-	_	-	-	-	-	-	(612)	(1190)
Dy	Ho + DyF = HoF + Dy	(19)	555.6	578.2	-	-	HoF (566.4)	(546)	(1128)
Но	Ho + SmF = HoF + Sm	(20)	571.2	564.6	-	-	SmF (567.1)	(566.4)	1141.0
	Ho + EuF = HoF + Eu	(21)	546.2	567.3	-	-	EuF (549.4)		_
	$3\text{HoF} = 2\text{Ho} + \text{HoF}_3$	(22)	563.3	562.1	-	-	HoF ₃ (1769.7)		_
	$HoF_2 + Ho = 2HoF$	(23)	-	-	1141.0	1139.1	HoF (566.4)	-	_
	$3\text{HoF}_2 = 2\text{HoF}_3 + \text{Ho}$	(24)	-	-	1133.8	1152.3	HoF ₃ (1769.7)	-	_
Er	HoF + Er = Ho + ErF	(25)	580.6	586.6	-		HoF (566.4)	(585)	1157.1
	$HoF_2 + Er = Ho + ErF_2$	(26)	-	-	1157.1	1161.5	HoF ₂ (1141.0)	-	_
Tm	Tm + CaF = TmF + Ca	(28)	518.7	516.9	-	-	CaF (530.0)	518.7	1095.4
	$TmF + CaF = TmF_2 + Ca$	(29)	-	-	1095.4	1071.6	TmF (518.7), CaF (530.0)	-	-
	$TmF + TmF_3 = 2TmF_2$	(30)	_	_	1091.7	1077.3	TmF (518.7), TmF ₃ (1703.8)	-	-
Yb	-	_	-	_	-	-	-	(491)	(1072)
Lu	-	-	-	-	-	-	-	(632)	(1203)

^a The enthalpy of atomization assigned to a given compound is given in parentheses.
 ^b The enthalpies of atomization calculated from the enthalpies of reaction determined by the third law are given in the fourth and sixth columns; analogous data calculated from the enthalpies of reaction determined by the second law are listed in the fifth and seventh columns.



FIGURE 46 $\Delta_{at}H^{\circ}(RF, 0)/\Delta_{at}H^{\circ}(RCl, 0)$ versus n (n = 1-15 for R = La-Lu). Solid line, approximating polynomial; \Box , value obtained from $\Delta_{at}H^{\circ}(0, III law)$; and \blacktriangle , value obtained from $\Delta_{at}H^{\circ}(0, III law)$. The electronic contribution to the thermodynamic functions of RF was determined from the excitation energies of the RX molecules (R = La-Lu). Reproduced from Chervonnyi and Chervonnaya (2007f) with permission from Pleiades Publishing, Ltd.

Figure 46 is somewhat different from Figure 45 for which all specific features have been discussed above. The approximating polynomial, which provides the same accuracy in both cases, was derived from a smaller number of data points. The procedure includes data on lanthanum (third law), neodymium (third law), samarium (third law), europium (second law), and thulium (third law) monohalides. The resulting polynomial,

$$\frac{\Delta_{\rm at}H^{\circ}(\rm RF,0)}{\Delta_{\rm at}H^{\circ}(\rm RCl,0)} = 1.26451 + 0.00665n - 1.41844 \times 10^{-5}n^2 \tag{39}$$

and the enthalpies of atomization of RCl (eighth column, Table 74) were used for estimating the $\Delta_{at}H^{\circ}(RF, 0)$ values. We were mainly interested in selecting a reasonable value for $\Delta_{at}H^{\circ}(HoF, 0)$ from the results of these calculations. Indeed, the $\Delta_{at}H^{\circ}(HoF, 0)$ estimated value (566.4 kJ/mol) nearly coincides with the average value (567.5 kJ/mol) found from the five values for reactions (20)–(22). We were not able to extract additional information from Table 77. The use of the other set of thermodynamic functions of RF for processing the results for heterogeneous reactions led (as previously) to underestimated values of the enthalpies of atomization of corresponding monofluorides. Therefore, we used the estimated value of the enthalpy of atomization of HoF as the reference value in calculations for reactions involving gadolinium, dysprosium, and erbium fluorides.

There are three noticeable differences between Figures 45 and 46. First, in Figure 46, the enthalpy ratio for ErX (third law) does not fit into the polynomial dependence (39); better agreement is observed for the same ratio found by the second law. Second, both ratios obtained from second and third laws for DyX are considerably higher than the values calculated by Eq. (39). On the other hand, in Figure 45, the corresponding points fall on the polynomial curve (37). Third, none of the ratios for GdX is consistent with the value calculated by Eq. (39), whereas Figure 45 shows that the ratio calculated from the enthalpy of atomization of GdF found by the second law falls on the corresponding polynomial curve.

Since there is only a small number of reactions involving monofluorides suitable for calculation of $\Delta_{at}H^{\circ}(RF_2, 0)$, the change in the set of thermodynamic functions of RF has virtually no effect on recommended $\Delta_{at}H^{\circ}(RF_2, 0)$ values. Differences are no more than 3 kJ/mol.

Considering the differences caused by the substitution of one set of thermodynamic functions of RF for the other, we should emphasize that, in our opinion, the equilibrium constants of reactions involving dysprosium, holmium, and erbium and their monofluorides (Zmbov and Margrave, 1966c) are quite reliable. If some doubts may rise, they refer to the experimental data for reactions (16)–(18) (Zmbov and Margrave, 1967a), consistent with the difficulties of measuring the equilibrium constants of these reactions mentioned previously.

We believe that all the above differences are related to the quality of the thermodynamic functions of lanthanide monohalides. In particular, the changes in the enthalpies of atomization of gadolinium, dysprosium, and holmium fluorides, which were revealed despite the simultaneous change in the enthalpy of atomization of the corresponding monochlorides, are caused by different values of the electronic contribution calculated by different methods (see Figures 41 and 42 in Section 10). This phenomenon is more pronounced for monochlorides (Table 75). For monochlorides, not only the entire set of the measured equilibrium constants but also data obtained by an independent method, in particular electron impact (Sapegin, 1984), are available. The uncertainty on the nature of the calculated lowest-lying atomic multiplet state of R^+ in R^+X^- for some RF and RCl (Kaledin et al., 1996a) is noteworthy, but it is not decisive for estimating the electronic correction.

It is worth noting that the $\Delta_{at}H^{\circ}(RF, 0)$ values listed in the ninth column of Table 76 and in Table 79 are considerably different: for example, this difference is +17.6 kJ/mol for LaF and -102.6 kJ/mol for LuF. We have to mention that Table 79 contains data from Kaledin et al. (1999)

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
661.5 Th	618.5 Dv	579.0 Ho	545.5 Er	557.5 Tm	561.0 Yb	539.5 Lu	591.0 -
642.4	527.6	514.4	569.4	506.0	521.6	520.4	_

TABLE 79 Enthalpies of atomization (kJ/mol) of RF

Taken from Kaledin et al. (1999).

which originate from the conclusions about the multiplet states of R^+ in R^+X^- (see Kaledin et al., 1996a).

It is evident that the use of the energies of the electronic states of R^+ from Martin et al. (1978) for estimating the contribution from electronic excitation to the reduced Gibbs energy of RX is not quite adequate since this approach ignores the perturbation of the energy levels of R^+ by the X^- ligand field. However, the attempts to consider this perturbation by Kaledin et al. (1996a) should unfortunately be deemed as unreliable. This is not related to the quality of calculations.

As is known, the development of the LFT (Field, 1982) made it possible to refine the enthalpies of atomization of lanthanide monoxides and to elucidate their behavior for RO (Dulick et al., 1986). However, when comparing the performance of different methods, including DFT, for describing the chemical bond in RX, some authors (Heiberg et al., 2003; Wang and Li, 2002) arrived at the conclusion that it is currently impossible to adequately describe the role of the 4f shell in chemical bonding. All corollaries from such a description are qualitative. Among RX molecules, accurate calculations of electronic excitation have only been performed for LaX (Fahs et al., 2002, 2004; see Section 10 for details).

Recommended data for thermochemical properties of RX(g) and RF₂(g)

The enthalpies of atomization and formation recommended by us are summarized in Tables 80 and 81 for standard temperatures 0 and 298.15 K.

11.8 IEs of RX molecules

The initial estimates of IE(RCl) for EuCl (Hariharan and Eick, 1972) and YbCl (Hariharan et al., 1972) were performed assuming that, as in the case of alkaline-earth monochlorides, this characteristic parameter is ~ 0.2 eV lower than the corresponding IE(R) value. The correctness of these

	RCl(g)				RF(g)				
R	$\Delta_{at} \mathcal{H}^{\circ}$ (0)	$\Delta_{at} \mathcal{H}^{\circ}$ (298)	$\Delta_{ m f}$ H $^{\circ}$ (0)	$\Delta_{ m f}$ H $^{\circ}$ (298)	$\Delta_{ m at} {\it H}^{\circ}$ (0)	$\Delta_{at} \mathcal{H}^{\circ}$ (298)	$\Delta_{ m f}$ H $^{\circ}$ (0)	$\Delta_{ m f}$ H $^{\circ}$ (298)	
La	506.9	508.968	43.063	42.334	643.9	647.472	-136.282	-138.092	
Ce	490.1	493.030	48.520	45.346	626.4	630.093	-130.125	-133.639	
Pr	470.2	472.363	6.420	4.752	604.4	607.326	-170.125	-172.133	
Nd	448.2	450.471	-0.580	-2.040	579.6	582.634	-174.325	-176.125	
Pm	436.0	438.221	-56.380	-57.756	566.3	569.288	-229.025	-230.745	
Sm	431.4	434.637	-106.780	-107.738	555.7	559.705	-273.425	-274.728	
Eu	419.1	421.681	-121.480	-124.192	549.5	552.869	-294.225	-297.302	
Gd	466.9	469.936	52.720	49.877	614.6	618.408	-137.325	-140.517	
Tb	457.1	461.227	50.520	46.131	604.5	609.402	-139.225	-143.966	
Dy	411.7	414.389	-4.080	-7.835	546.5	549.957	-181.225	-185.325	
Ho	418.4	420.949	3.220	0.544	557.5	560.828	-178.225	-181.257	
Er	429.1	431.463	5.520	3.666	574.0	577.140	-181.725	-183.933	
Tm	383.7	385.972	-30.080	-31.911	514.5	517.555	-203.225	-205.416	
Yb	361.2	363.834	-88.580	-90.046	485.9	489.335	-255.625	-257.469	
Lu	461.9	464.732	85.720	84.432	623.1	626.717	-117.825	-119.475	

TABLE 80 Recommended enthalpies of atomization and enthalpies of formation for RX, kJ/mol^a

^{*a*} All primary (experimental) enthalpy values are given with an accuracy of 0.1 kJ/mol. Other values calculated from them have an accuracy of 0.001 kJ/mol, as accepted in IVTANTERMO (2004).

R	$\varDelta_{at}H^{\circ}(0)$	⊿ _{at} H°(298)	⊿ _f H°(0)	⊿ _f H°(298)
La	1271.3	1277.274	-686.407	-688.514
Ce	1249.5	1254.804	-675.950	-678.970
Pr	1214.2	1219.275	-702.650	-704.702
Nd	1175.6	1180.787	-693.050	-694.898
Pm	1169.8	1175.399	-755.250	-757.476
Sm	1159.8	1165.891	-800.250	-801.534
Eu	1143.1	1149.229	-810.550	-814.282
Gd	1213.5	1219.805	-658.950	-662.534
Tb	1191.5	1197.890	-648.950	-653.074
Dy	1130.2	1135.726	-687.650	-691.714
Ho	1142.2	1147.481	-685.650	-688.530
Er	1155.3	1159.748	-685.750	-687.161
Tm	1095.5	1100.770	-706.950	-709.251
Yb	1075.1	1081.314	-767.550	-770.068
Lu	1206.0	1212.197	-623.450	-625.575

TABLE 81 Recommended enthalpies of atomization and enthalpies of formation for $RF_2(g)$, kJ/mol^a

^{*a*} All primary (experimental) enthalpy values are given with an accuracy of 0.1 kJ/mol. Other values calculated from them have an accuracy of 0.001 kJ/mol, as accepted in IVTANTERMO (2004).

estimates was supported by measurements of IE(RCl) by the electronimpact method for R = Sm, Eu, Dy, Tm, and Yb (Sapegin, 1984).

To obtain IE(RCl) values for the entire RCl series, we used the following procedure. Taking into account the known appearance energies of RCl⁺ ions that form during the dissociative ionization of RCl₂ (AE(RCl⁺/ RCl₂)) and RCl₃ (AE(RCl⁺/RCl₃)) (see, for instance, Chervonnyi and Chervonnaya, 2004a,b,e,f, 2005b; Hastie et al., 1968; Hariharan and Eick, 1972; Hariharan et al., 1972; Sapegin, 1984), we used the following relationships:

$$IE(RCl) = AE(RCl^+/RCl_3) - D^{\circ}(Cl_2R - Cl, 0) - D^{\circ}(ClR - Cl, 0)$$

and

$$IE(RCl) = AE(RCl^+/RCl_2) - D^{\circ}(ClR - Cl, 0)$$

where $D^{\circ}(0)$ is the bond dissociation energy in the corresponding molecules.

The necessary $D^{\circ}(\text{Cl}_2\text{R}-\text{Cl}, 0)$ and $D^{\circ}(\text{ClR}-\text{Cl}, 0)$ values were calculated from $\Delta_{\text{at}}H^{\circ}(\text{RCl}_3, 0)$, $\Delta_{\text{at}}H^{\circ}(\text{RCl}_2, 0)$, and $\Delta_{\text{at}}H^{\circ}(\text{RCl}, 0)$. As a result, we obtained from one to five IE(RCl) values for each monochloride. For most compounds, the scatter of IE(RCl) values for a given monochloride is relatively small (~0.2–0.3 eV). Exceptions are AE(LaCl⁺/LaCl₃) and AE

 $(EuCl^+/EuCl_3)$ data from Hastie et al. (1968), which lead to very high ionization energies IE(LaCl) and IE(EuCl) as compared to the other values. These data were consequently excluded from further averaging.

The remaining IE(RCl) values were averaged taking into account the trends in the behavior of IE(R) and IE(Ba) from NIST Ground Levels. The inclusion of barium in the series under consideration is due to the fact that its electronic structure can be represented as $4f^{0}5d^{0}6s^{2}$. As follows from Martin et al. (1978) and Cao and Dolg (2002), all lanthanides in the gaseous state have two electrons in the 6s shell. Lanthanum, cerium, gadolinium, and lutetium also have one electron in the 5d shell. The R⁺ (and Ba⁺) ion is formed, as a rule, through the loss of one s electron. In the resulting lanthanum and cerium ions, the second s electron is transferred to the 5d level. In lutetium, both 6s electrons are retained, while the 5d electron is lost. For most elements, these specific features of ionization lead to a linear dependence of the IE on *k*:

 $(5.13826 \pm 0.01564) + (0.07366 \pm 0.0016)k,$

where k = 1-16 for Ba, La–Lu.

The IE(La), IE(Ce), and IE(Gd) values are above, and the IE(Lu) value is below this approximating line.

Analysis of the calculated ionization energies IE(RCl) and IE(BaCl) from IVTANTERMO (2004) showed that all IE values for PrCl, NdCl, SmCl, EuCl, DyCl, TmCl, YbCl, and BaCl (a total of 32 values) are also approximated with high accuracy by a linear function:

$$(4.91652 \pm 0.09099) + (0.07075 \pm 0.0089)k.$$

From these data, the IE(RCl) values for the above RCl and IE(PmCl) were calculated and are reported in the fifth column of Table 82. The choice of such a RCl series is due to the intention not to lose the specific features in the variation of IE(RCl) with R (see Kaledin et al., 1999) for some monochlorides in the series being analyzed.

The IEs of RCl not included in the above series were determined by averaging available values for each of them. For LaCl, four values were averaged, and for GdCl and HoCl, three values were averaged. For CeCl, TbCl, and LuCl, the values calculated from the experimental AE(RCl⁺/RCl₃) data were taken as IEs. The exception is IE(ErCl): the value calculated from AE(ErCl⁺/ErCl₃) (6.18 eV) clearly falls out of the above linear dependence of IE(RCl). As we have shown previously (Chervonnyi and Chervonnaya, 2007g), among the lanthanide chlorides studied by Sapegin (1984), the most unreliable data were obtained for ErCl₃. Even the ionization and appearance energies for LuCl₃ determined with a large experimental error by Hastie et al. (1968) seem to be more reliable. For example, it is worth noting that IE(LuCl₃) = 11.5 ± 0.5 eV determined by Hastie et al. (1968) coincides, within 0.5 eV, with the vertical IE (11.55 ± 0.04 eV)

М	IE(MCl)	AE(MCl ⁺ /MCl ₂)	AE(MCl ⁺ /MCl ₃)	IE(MCl)
1	2	3	4	5
Ва	4.9645 ^a	_	_	
La	-	10.52 ± 0.07^b	16.12 ± 0.08^b	5.35
	-	-	16.04 ± 0.07^{b}	
	-	-	16.2 ± 0.1^{c}	
	-	-	17.5 ± 1^{d}	
Ce	-	-	15.92 ± 0.07^{b}	5.31
Рг	-	10.18 ± 0.06^{b}	15.36 ± 0.09^{b}	5.23
	-	-	15.41 ± 0.08^{b}	
Nd	-	10.32 ± 0.68^{b}	15.02 ± 0.07^{b}	5.29
	-	_	15.24 ± 0.06^{b}	
Pm	-	_	_	5.34
Sm	5.45 ± 0.07^{b}	10.26 ± 0.06^{b}	14.28 ± 0.07^{b}	5.40
	-	10.22 ± 0.05^{b}	14.2 ± 0.1^{e}	
Eu	5.40 ± 0.08^{b}	10.29 ± 0.07^{b}	18.0 ± 0.5^d	5.43
	$5.5 \pm 0.1^{f,g}$	$10.24 + 0.05^{b}$	_	
	-	$9.9 \pm 0.1^{f,g}$	-	
	_	10.5 ± 0.5^d	_	
	_	11.0 ± 0.5^{d}	_	
Gd	_	10.92 ± 0.07^{b}	16.02 ± 0.07^{b}	5.90
	_	-	16.21 ± 0.08^{b}	
Tb	_	-	15.84 ± 0.07^b	5.67
Dy	5.77 ± 0.05^{b}	10.54 ± 0.08^{b}	15.39 ± 0.05^{b}	5.69
Ho	_	10.79 ± 0.06^{b}	15.55 ± 0.07^{b}	5.85
	_	-	15.63 ± 0.06^{b}	
Er	_	-	15.82 ± 0.07^{b}	(6.00)
Tm	6.00 ± 0.05^{b}	10.82 ± 0.07^{b}	15.30 ± 0.06^{b}	5.92
Yb	6.05 ± 0.06^{b}	$10.76 + 0.08^{b}$	14.60 ± 0.05^{b}	5.99
	_	10.56 ± 0.04^{b}	14.3 ± 0.1^{h}	
	_	11.1 ± 0.1^{h}	_	
	_	10.70 ± 0.21^{i}	_	
Lu	-	-	16.0 ± 0.5^d	5.59

 TABLE 82
 Ionization energies for BaCl and the entire RCl series and appearance
 energies of RCl^+ ions formed during dissociative ionization of RCl_2 and RCl_3 (eV)

^a IVTANTERMO (2004).

^a IVTANTERMO (2004).
 ^b Sapegin (1984).
 ^c Chervonnyi and Chervonnaya (2004b).
 ^d Hastie et al. (1968).
 ^e Chervonnyi and Chervonnaya (2004e).
 ^f Chervonnyi and Chervonnaya (2004b).
 ^g Chervonnyi and Chervonnaya (2004b).

^{*h*} Chervonnyi and Chervonnaya (2004f).

^{*i*} Hariharan et al. (1972).

of this compound measured by X-ray photoelectron spectroscopy (Lee et al., 1982). As for ErCl, we can assume, based on the analysis of all data on dysprosium, holmium, and erbium chlorides from Sapegin (1984), that the IE(ErCl) value does not exceed 6.0 eV. It follows from the data listed in the fifth column of Table 82 that, for all RCl molecule, the difference IE (R) – *IE*(RCl) is positive, except for R = Lu. The average value of this difference is 0.22 ± 0.04 eV. For lutetium, this difference is negative (-0.16 eV).

The available experimental values of IE(RF) can be classified into two groups. The first group (second column, Table 83) contains the data for R = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Tm collected by several authors (Hildenbrand and Lau, 1995; Kleinschmidt et al., 1981; Zmbov and Margrave, 1966a,c, 1967a, 1968) for demonstrating the molecular nature of RF⁺ ions. The accuracy of these data is low and is estimated by the authors to be around ± 0.3 eV. The second group of data (third column,

R	IE(RF) ^a	IE(RF) ^b	$\Delta_{at} \mathcal{H}^{\circ}(RF^+,0)^{c}$	$\Delta_{at} \mathcal{H}^{\circ}(RF^+, 0)^d$
1	2	3	4	5
La	5.0	(5.45)	656.2	(694.7)
Ce	_	(5.50)	630.1	(678.4)
Pr	_	(4.80)	668.5	_
Nd	5.0	4.91	638.9	_
Pm	_	(5.00)	622.5	_
Sm	4.8, 5.7	5.09	609.1	_
Eu	5.1, 5.9	5.21	593.9	_
Gd	6.2	6.16	613.7	(670.6)
Tb	_	6.13	578.8	(648.3)
Dy	6.0	5.55	584.0	_
Ho	6.2, 6.1	6.02	557.7	(596.2)
Er	6.3	6.31	554.5	(597.9)
Tm	5.8	5.87	544.8	_
Yb	_	5.90, 5.91	519.1	_
Lu	_	(6.90)	480.9	(586.0)

TABLE 83 Ionization energies (eV) for RF and enthalpies of atomization (kJ/mol) for RF^+

^{*a*} Determined by Hildenbrand and Lau (1995), Zmbov and Margrave (1966a, c, 1967a, 1968), and Kleinschmidt et al. (1981) before measuring K_{p}^{c} . ^{*b*} Measured by Kitaev et al. (1988a,b,c) and Belyaev et al. (1996); the values estimated from these measurments

^b Measured by Kitaev et al. (1988a,b,c) and Belyaev et al. (1996); the values estimated from these measurments are given between parentheses.

^c Calculated by an equation analogous to Eq. (40) with the use of IE(R) from NIST Ground Levels and IE(RF) from the third column of this table.

 d Values in parentheses are the enthalpies of atomization calculated with the use of IE(RF) estimated from the linear dependence on $R_{\rm e}^{-4}$.
Table 83) comprises the experimental values of IE(RF) for most compounds of this series (except LaF, CeF, PrF, PmF, and LuF). These values were obtained when studying the ionization processes of RF (Kitaev et al., 1988a,b,c) and from analysis of spectroscopic data aimed at the determination of IE(RF) (Belyaev et al., 1996). The accuracy specified in these works is better (± 0.07 eV). Missing data (parenthesized in the third column of Table 83) were estimated by Kitaev (1988) and Gotkis (1988, 1991) who relied on the data reported by Kitaev et al. (1988a,b,c) and Belyaev et al. (1996) and who made use of the model of 4f electron transfer induced by the ligand field.

11.9 Atomization enthalpy of RX^+ ions

The $\Delta_{at}H^{\circ}(RCl, 0)$ and IE(RCl) values obtained in this work, as well as the IE(R) values from NIST Ground Levels, allow us to calculate the enthalpies of atomization of RCl⁺ ions by the equation

$$\Delta_{\mathrm{at}}H^{\circ}(\mathrm{RCl}^{+},0) = \mathrm{IE}(\mathrm{R}) + \Delta_{\mathrm{at}}H^{\circ}(\mathrm{RCl},0) - \mathrm{IE}(\mathrm{RCl}).$$
(40)

The results are summarized in Table 84. The plot of $\Delta_{at}H^{\circ}(RCl^+, 0)$ versus the atomic number of a 4f element (*n*) is a broken line with maxima at LaCl⁺, GdCl⁺, and LuCl⁺ and minima at EuCl⁺ and YbCl⁺. In addition,

R	$\Delta_{at} \mathcal{H}^{\circ}(RCl^+, 0)^{a}$	$\Delta_{ t at} {m {\cal H}^{\circ}}({ t RF^+},{ t 0})$
La	528.8	694.7
Ce	512.2	678.4
Pr	492.8	668.5
Nd	470.9	638.9
Pm	459.3	622.5
Sm	454.9	609.1
Eu	442.3	593.9
Gd	491.0	670.6
Tb	475.8	648.3
Dy	435.7	584.0
Ho	435.0	596.2
Er	439.5	597.9
Tm	409.2	544.8
Yb	386.7	519.1
Lu	446.1	586.0

TABLE 84 Enthalpies of atomization for RF⁺, and RCl⁺ (kJ/mol)

^a Calculated by Eq. (40) with the use of IE(R) from NIST Ground Levels and IE(RCI) from the fifth column of Table 82

this curve demonstrates an increase in the enthalpy of atomization on going from DyCl⁺ to ErCl⁺; that is, these data reflect the double periodicity of properties, which is typical of other series of similar 4f compounds.

The $\Delta_{at}H^{\circ}(RF^+, 0)$ values calculated using IE(R) from NIST Ground Levels and the IE(RF) values from the third column of Table 83 lead to results (fourth column, Table 83) radically different from the $\Delta_{at}H^{\circ}$ (RCl⁺, 0) values. No pronounced double periodicity is observed for $\Delta_{at}H^{\circ}(RF^+, 0)$ as a function of *n*. To elucidate the reasons for this behavior, we examined the $\Delta_{at}H^{\circ}(RF^+, 0)/\Delta_{at}H^{\circ}(RCl^+, 0)$ ratios for the entire series of 4f elements. Our analysis showed that the estimates of IE(RF) for LaF, CeF, and LuF (Gotkis, 1988, 1991; Kitaev, 1988) and experimental values for GdF and TbF (Kitaev et al., 1988b) are overestimated. Conversely, the IE of LaF (Chervonnyi and Chervonnaya, 2007c), which is 0.45 eV lower than the value estimated by Kitaev (1988) and Gotkis (1988, 1991), seems to be more reliable. It is worth noting in this context that some $\Delta_{at}H^{\circ}$ (RF⁺, 0) values listed in the fourth column of Table 83 are not sufficiently reliable.

On the other hand, it has been shown (Belyaev et al., 1990, 1996) that the ionization energies IE(MX) of diatomic molecules (M is an alkalineearth metal, and X is F, Cl, Br, I, OH, and O) formed by the same cation and different anions are described by a linear dependence on R_e^{-4} . The IE (M) value falls on the same line at $R_e = \infty$. Application of this approximation to IE(R), IE(RF), and IE(RCl) showed that it holds true for these compounds in half of the cases only, deviation from linearity being observed for La, Ce, Gd, Tb, Ho, Er, and Lu and their compounds.

The calculation of IE(RF) from the available IE(R) and IE(RCl) data, according to the dependence given by Belyaev et al. (1990, 1996), yields the following values (eV): 5.05 (LaF), 5.00 (CeF), 5.57 (GdF), 5.41 (TbF), 5.62 (HoF), 5.86 (ErF), and 5.81 (LuF).

The dependences of IE(M) (M = Ba, La–Lu) and IE(MX) (X = F, Cl) values versus k are depicted in Figure 47.

Table 83 presents the recommended $\Delta_{at}H^{\circ}(RX^+, 0)$ values. Calculation of $\Delta_{at}H^{\circ}(RF^+, 0)$ (parenthesized values in the fifth column of Table 83) from these IE(RF) values gives the atomization enthalpies that exhibit a clearly pronounced double periodicity. The introduction of such corrections seems therefore to be justified. Indeed, there are no convincing arguments to believe that the substitution of one ligand (Cl⁻) for another similar one (F⁻) leads to a radical change in the bond energy for some 4f elements.

In addition to $\Delta_{at}H^{\circ}(RX^+, 0)$ values, IE(RX) data should be determined and described for a detailed analysis of the available experimental data, which pertains to the following aspects.

The combination of Knudsen's technique of sublimation (evaporation) of the mixtures of compounds with mass spectrometric monitoring of the



FIGURE 47 Dependences of (1) IE(M), (2) IE(MCI), and (3) IE(MF) versus k. Black dots (\bullet) represent our estimates of IE(RF).

products in the gas phase is widely used in thermodynamic studies. The partial pressures p_i of the species i at temperature T result from the relation $p_i = kI_iT/\sigma_i$, where k is the pressure calibration factor, I_i is the measured ion current, and σ_i is the ionization cross section of the *i*th component. The equilibrium constants (K_p°) are calculated from observed ion intensities corrected for the ionization cross section of the *i*th component. It is clear that one of the sources of the large errors in the calculation of the K_p° values is the uncertainty in the ionization cross sections used in the conversion of mass spectrometric ion intensities into absolute values of partial pressure. Another often used procedure is the measurement of equilibrium constants of the isomolecular reactions, for which the additivity scheme of ionization cross section calculation is assumed to introduce the smallest error into equilibrium constants.

We have demonstrated (Chervonnyi, 2009, 2010) that a key factor in the conversion of the primary ion current intensity of the individual gas component in absolute (or relative) value of its partial pressure is to ensure that adequate conditions of measurement of the ionic currents in near-threshold region are used (at energies of ionizing electrons of 3–5 eV above the IE neutral components of the investigated reaction). Failure to do so can lead to noticeable errors. This is particularly evident in the calculation of the reactions with stoichiometric coefficients greater than unity, as shown in Table 85 for the processing of the experimental data reported by Markus (2002).

Reaction	Molecule	$\Delta_{at} \mathcal{H}^{\circ}$ (0)			
AlO = Al + O	AlO	$510.7 \pm 3.3^{a,b}$	507 ± 5 ^c	510 ± 10^{d}	484.1 ^e
$Al_2O = 2Al + O$	Al ₂ O	$1067.2 \pm 6.9^{a,b}$	$1050 \pm 25^{\circ}$	1065.7 ± 17^{d}	1011.8 ^e
$\begin{array}{l} Al_2O_2=2Al\\ +\ 2O \end{array}$	Al_2O_2	$1556.7 \pm 9.9^{a,b}$	1550 ± 50^c	1572.9 ± 19^{d}	-

TABLE 85 Enthalpies of atomization ($\Delta_{at}H^{\circ}(0)$, kJ/mol)

^a Chervonnyi (2009).

^b Chervonnyi (2010).

^c Gurvich et al. (1978–1984). ^d Milushin et al. (1987)

^e Markus (2002).

For estimating the quality of measurements of equilibrium constants for reactions involving RF molecules (Hildenbrand and Lau, 1995; Kleinschmidt et al., 1981; Zmbov and Margrave, 1966a,c, 1967a, 1968), it is presumably correct to compare data in Table 83 on the basis of the criterion of equal distances to the corresponding ionization threshold determined by measurement of the ion current of each component of the reactions, rather than on the basis of the discrepancy between the corresponding values listed in the second and third columns of Table 83. Despite the simple equipment used for recording ionization efficiency curves and an unsophisticated method of determination of the appearance energy thresholds of the corresponding ions in mass spectra (Zmbov and Margrave, 1966a,c, 1967a), the same authors (Zmbov and Margrave, 1966b) were able to determine IE(R) with sufficient accuracy for the determination of K_{p}° . The differences (in eV) between the recommended values from NIST Ground Levels and those from Zmbov and Margrave (1966b) are indeed small: Sm (+0.08), Eu (+0.06), Gd (+0.17), Dy (+0.16), Ho (+0.17), Er (0.00), Tm (+0.31), and Yb (+0.35).

Violation of the criterion of equal distances to the corresponding ionization threshold is observed for the reaction of holmium with DyF (about 0.5 eV) (see Zmbov and Margrave, 1966c) and for the reactions of holmium with SmF and EuF (about 1 eV) (see Zmbov and Margrave, 1967a). The same is observed for the reactions of barium with LaF and LaF₂ (about 0.5 eV) (see Hildenbrand and Lau, 1995). However, according to Table 76, this violation had no effect on the results for reaction (19), although it could be among the factors that had an impact on the results for reactions (20) and (21).

11.10 Recommended thermodynamic functions for RX molecules

The results of calculation of the thermodynamic functions obtained by all methods (see Section 10) are listed in Tables A9–A13 in the form of the coefficients of the polynomial (12).

Our findings show that the thermodynamic functions (Tables A10 and A12) of RCl and RF (R = Ce–Lu) in which the electronic contribution is determined from the excitation energies of R⁺ ions are more reliable for the description of high-temperature equilibria. The corresponding error, calculated from comparison of the $\Delta_{at}H^{\circ}(0, \text{EI})$ and $\Delta_{at}H^{\circ}(0, \text{III law})$ values (Table 75), is not larger than $\pm 3 \text{ J/(mol·K)}$. The thermodynamic functions for LaCl and LaF (Table A9) are found by direct summation over the energy levels and recommended for use in thermodynamic calculations of equilibria involving these molecules.

12. CORRELATION OF THERMODYNAMIC PROPERTIES OF LANTHANIDE HALIDES

A comparison between thermodynamic functions for the 4f element trihalides in the gas and condensed states mostly cited in the literature (Barin, 1995; Myers and Graves, 1977a) and their consistent description documented in this work shows that in all cases, the values of the reduced Gibbs energy were substantially adjusted in this new approach. The implemented corrections originate mainly from two factors. First, the electronic contribution (Φ_{el}) was calculated more accurately by taking into account the splitting of the ground state in the ligand field. Further, since this component is strictly individual for each of the lanthanides, we took into account its contribution in the calculation of the thermodynamic functions for the condensed state. Second, marked changes were introduced in other components of the reduced Gibbs energy. Another symmetry number ($\sigma = 3$ instead of 6) was taken into account in the calculation of the thermodynamic functions for molecules in the rigid rotator-harmonic oscillator approximation. For the condensed state of the compound, we used values of characteristic parameters obtained from correlations of these parameter with the molar volume. Note however that these parameters are sometimes not consistent with those obtained from experimental data.

In the subsequent analysis of the heterogeneous (sublimation/evaporation) and homogeneous (gas-phase reaction) equilibria, we have shown that the reduced Gibbs energy has a relatively low error (not exceeding 2–3 J/(mol·K)) provided a sufficiently high degree of convergence between the $\Delta_{sub}H^{\circ}(298, \text{III law})$ and $\Delta_{sub}H^{\circ}(298, \text{II law})$ values. Such agreement is reached when the complete set of experimental data and empirical relationships between different physical and chemical properties of the lanthanide trihalides are used.

Since the initial experimental data for reduced Gibbs energy calculations were most reliable for lanthanide trifluorides, we restricted ourselves to considering heterogeneous equilibria only for these compound, especially that data obtained by McCreary and Thorn (1973a,b, 1974a,b) could obviously be singled out. The accuracy for sublimation enthalpies was ensured thanks to the procedure developed by Thorn (1971) for estimating the correctness of saturated vapor pressures by comparing the $\Delta_{sub}H^{\circ}(T)$ (or $\Delta_{vap}H^{\circ}(T)$) and $\Delta_{sub}S^{\circ}(T)$ (or $\Delta_{vap}S^{\circ}(T)$) values calculated according to the second law of thermodynamics. As a consequence, we relied on the data from McCreary and Thorn (1973a,b, 1974a,b) for performing our analysis. The close agreement between the $\Delta_{sub}H^{\circ}$ (298, III law) and $\Delta_{sub}H^{\circ}$ (298, II law) values obtained from these data is by itself evidence of satisfactory accuracy of the suggested thermodynamic functions.

We found that the reliability of data on lanthanide di- and trichlorides was substantially lower. This can be explained by the lower stability of these compounds (compare Figures 48 and 49) resulting in difficult syntheses of pure substances with the required stoichiometry, as well as by their well-defined propensity for hydrolysis. Taking this into account, we abandoned the use of the Thorn's procedure (Thorn, 1971) and performed calculations on the basis of virtually all the experimental data available. We assumed that the presence of small amounts of either highor, conversely, low-volatility impurities that distorted the slope of the corresponding semilogarithmic anamorphosis plots could not influence $\Delta_{sub}H^{\circ}(298, III law)$ substantially. A small number of data was, however, rejected by Chervonnyi and Chervonnaya (2007g), their reliability being low.



FIGURE 48 Enthalpies of formation for the crystalline lanthanide trifluorides.



FIGURE 49 Enthalpies of formation for the crystalline lanthanide trichlorides.

In this way, it was possible not only to obtain the appropriate variation of the $\Delta_{sub}H^{\circ}(298)$ values for the entire series of RCl₃ but also to ensure that the proposed method for calculating heat capacities of condensed state leads to realistic values of the reduced Gibbs energy.

We were forced to use the quasi-harmonic approximation for describing the temperature dependence of heat capacity. Already prior to calculations, it was clear that the approximation of experimental data, part of which was not very accurate, should be performed by varying a minimum number of characteristic parameters with predictable behavior. In this respect, the quasi-harmonic approximation is optimum, although it ensures a correct heat capacity description only at temperatures lower than ~0.5 $T_{\rm m}$ (see Oganov et al., 2002). A reliable description over the whole temperature range was obtained by introducing a correction $C_{\rm d,cor}^{\circ}(T)$ determined from measurements of high-temperature enthalpy increments or heat capacities at $T > ~0.5T_{\rm m}$. This allowed us to describe the heat capacity correctly up to the phase transition.

The model of volume-weighted interpolation of lattice contributions suggested by Westrum et al. (1989) was more recently substantiated in numerous experimental works (see the references in Sections 4 and 5). Our approximation of the experimental data with the use of lattice contributions to the heat capacity of lanthanide trifluorides and the hexagonal trichlorides showed that this model could be used to describe the dependence of the characteristic parameters on the molar volume and CN

of the lanthanide cation. This in turn allowed us to find errors in several experimental data and to suggest a reliable, although approximate, method for recalculating the corresponding values.

It should also be stressed that the rules formulated above for characteristic parameters could only be unveiled after the subtraction of the contribution caused by excited 4f levels, which noticeably influenced the thermophysical properties of lanthanide compounds in the condensed state. The absolute value of this contribution to heat capacity at a given temperature is determined by the chemical nature of the ligands and generates a change in the positions of the energy levels, as well as a possible change in the associated statistical weights) of the lanthanide in the corresponding valence state. This results in a local change in the temperature dependence of heat capacity in going from one ligand to another, which changes both the enthalpy and reduced Gibbs energy in spite of the integral character of these values.

In view of this fact and taking into account the individual character of the temperature dependence of the excess electronic contribution to the heat capacity of lanthanide compounds, the estimates of the properties of one compound based on the experimental data of another one without consideration of 4f shell excited electronic states should be regarded with caution. Such an approach is, for instance, discernible in the data included in Barin's handbook (Barin, 1995).

The empirical correlations found for the lanthanide trihalides were later used in the description of the thermodynamic functions of RX₂(g) and RCl₂(cr, liq). However, in the last case, experimental data processing showed that the main reason for their low reliability is nonstoichiometric compositions of the RCl₂ samples. Although the possibility of formation of compounds with R in the R²⁺ state was shown for virtually the whole series of lanthanides (see Mikheev et al., 1992), attempts at synthesizing lanthanum, cerium, praseodymium, promethium, gadolinium, terbium, erbium, and lutetium dichlorides were unsuccessful. The reasons for this have been repeatedly investigated (Chervonnyi and Chervonnaya, 2005c; Johnson, 1969; Kim and Oishi, 1979; Meyer, 1988; Meyer and Meyer, 1992; Mikheev and Rumer, 1999; Mikheev et al., 1992) in particular by analyzing the thermodynamic stability of RCl₂ on the basis of the enthalpy of formation of RCl₂ from R and RCl₃ at 298 K.

According to Chervonnyi and Chervonnaya (2005c), the enthalpy of this reaction is only positive for La, Ce, Gd, and Lu. It follows that only dichlorides of these lanthanides are unstable in the condensed state. The development of methods for synthesizing these compounds will probably allow us to overcome these difficulties. At least, already at present, micro-amounts (<0.2 wt.%) of lanthanides in the oxidation state 2+ have been obtained in chloride melts by cocrystallization (Kulyukhin et al., 1999; Mikheev and Rumer, 1999; Mikheev, 2002; Mikheev et al., 2000, 2004a,b,

2005). This makes it possible to measure electronic excitation energies, which is of utmost importance for increasing the reliability of thermodynamic functions. Actually, these parameters and measurements of the low-temperature heat capacity are the main factors that determine the accuracy of the sought for values.

The insufficiency of the literature data determined the sequence with which the thermodynamic properties of lanthanide halides were considered in our work. We first described RF₃ (Chervonnyi and Chervonnaya, 2007a), next RCl₃ (Chervonnyi and Chervonnaya, 2007b), and, finally, RCl₂ (Chervonnyi and Chervonnaya, 2008a). This description was preceded by complex calculations of thermodynamic equilibria in the case of samarium, europium, and ytterbium chlorides (Chervonnyi and Chervonnaya, 2004a,e,f, 2005b).

In these studies, we tested various methods for selecting and estimating the necessary parameters for estimating heat capacity and other thermodynamic parameters. The reliability of the final results obtained for RF₃ and RCl₃ was proved by analyzing heterogeneous equilibria with the participation of these compounds and by considering data obtained by independent methods (Chervonnyi and Chervonnaya, 2007a,g). The trends in thermochemical parameter variations over the series of lanthanides (Chervonnyi and Chervonnaya, 2007a,b) were used in subsequent work (Chervonnyi and Chervonnaya, 2008b). Moreover, it was necessary to develop new approaches to reveal the rules governing property variations in the series of RCl₂ compounds and new methods for calculating and estimating missing values (see Chervonnyi and Chervonnaya, 2008b).

A widely used correlation of the thermodynamic properties of 4f element compounds is the dependence of the enthalpy of atomization on the atomic number of a 4f element (*n*). The plot of $\Delta_{at}H^{\circ}(R_2Cl_6, 0)$ versus *n* is a broken line with maxima at La₂Cl₆, Gd₂Cl₆, and Lu₂Cl₆ and minima at Eu₂Cl₆ and Yb₂Cl₆ (see Figure 50). In addition, this curve features an increase in the enthalpy of atomization in going from Dy₂Cl₆ to Er₂Cl₆; that is, the curve reflects the double periodicity observed for many lanthanide properties.

Similar relationships are shown in Figures 51 and 52 for $\Delta_{at}H^{\circ}(RX^{+}, 0)$, and in Figures 53 and 54 for $\Delta_{at}H^{\circ}(RX, 0)$.

From the data presented in the tables, it is easy to be convinced that a similar dependence is specific not only to $\Delta_{at}H^{\circ}(RX_2, 0)$ but also to $\Delta_{at}H^{\circ}(RX_3, 0)$.

The enthalpies of atomization of RX, RX₂, and RX₃ allow us to calculate the energies of successive bond dissociation in RX₃ molecules (Figures 53 and 54). In turn, these data lead to the conclusion that double periodicity is observed not only in the enthalpies of atomization of RX⁺, RX, RX₂, and RX₃ but also in X₂R—X bond dissociation energies. The energy of



dissociation of the second bond (XR-X) for chlorides remains virtually constant for all members of the 4f series. For fluorides, this energy monotonically decreases by \sim 30 kJ/mol.



FIGURE 52 Standard enthalpies of atomization of RCl⁺.



FIGURE 53 Energies of successive bond dissociation in RCl₃ molecules.

Similar relationships between the successive bond dissociation energies are explained by similar electronic structures of R in the mono- and divalent states. For most 4f elements, transition to the trivalent state is due to a change in the number of 4f electrons (see Cao and Dolg, 2002; Dolg



FIGURE 54 Energies of successive bond dissociation in RF₃ molecules.

and Stoll, 1996). It is worth noting that the occurrence of these relationships is an additional argument in favor of the correctness of the determination of the enthalpies of atomization of halides RX, RX₂, and RX₃.

The thermodynamic properties of lanthanide trifluorides, trichlorides, and dichlorides described in this work allow us to draw conclusions (Chervonnyi and Chervonnaya, 2008b, 2009) concerning the correlation of the thermodynamic properties of these compounds. Some special features of the variations in the enthalpy of sublimation over series of related compounds are well seen in the dependence of $\Delta_{sub}H^{\circ}(298)$ on the position of the lanthanide in the lanthanide series (Figures 55–57).

First, a decrease in the CN of a lanthanide ion in the crystal lattice of the corresponding compound leads to a lower $\Delta_{sub}H^{\circ}(298)$ value. This is observed in going from β -YF₃ (CN = 9) to LaF₃-type (CN = 6) structures of lanthanide trifluorides (Figure 55). A similar phenomenon is characteristic of lanthanide trichlorides (Figure 56) in going from UCl₃ (CN = 9) to YCl₃-type (CN = 6) structures. As follows from Figure 57, the enthalpies of sublimation of NdCl₂, PmCl₂, SmCl₂, and EuCl₂, which belong to PbCl₂-type lattices (CN = 9), are higher than the enthalpies of sublimation of DyCl₂, TmCl₂, and YbCl₂ (SrI₂-type lattices, CN = 7).

Next, the absolute value of the enthalpy of sublimation reflects the stability of the compound and its resistance to thermal transformations. Indeed, we have observed that samarium and europium trifluorides which have the lowest enthalpies of sublimation in the series of lanthanide trifluorides show a tendency to decompose at high temperatures



FIGURE 55 Standard enthalpies of sublimation of lanthanide trifluorides. Reproduced from Chervonnyi and Chervonnaya (2008b) with permission from Pleiades Publishing, Ltd.



FIGURE 56 Standard enthalpies of sublimation of lanthanide trichlorides. Reproduced from Chervonnyi and Chervonnaya (2008b) with permission from Pleiades Publishing, Ltd.



FIGURE 57 Standard enthalpies of sublimation of lanthanide dichlorides. Reproduced from Chervonnyi and Chervonnaya (2008b) with permission from Pleiades Publishing, Ltd.

(Chervonnyi and Chervonnaya, 2007a). The same tendency is characteristic of lanthanide trichlorides (Chervonnyi and Chervonnaya, 2007g): samarium and europium trichlorides with the lowest $\Delta_{sub}H^{\circ}(298)$ values decompose noticeably when heated, this being particularly true for EuCl₃ (see Chervonnyi and Chervonnaya, 2004a, 2005b).

Inverted trends are typical of lanthanide dichlorides. The least stable members of this series in the trivalent state have the highest stability in the divalent state. For instance, congruent vaporization is observed for samarium, europium, and ytterbium dichlorides over wide temperature ranges; vaporization proceeds with the formation of disproportionation products, but their partial pressures are lower by four and more orders of magnitude than the partial pressure of the major component in the vapor (see Chervonnyi and Chervonnaya, 2004a,e,f, 2005b). Conversely, for instance, the partial pressure of chlorine close to the melting point of europium trichloride is higher by a factor of ~10.

The shape of the curve shown in Figure 56 predicts a fairly high stability of neodymium and promethium dichlorides among the compounds with CN = 9 and dysprosium and thulium dichlorides among the compounds with CN = 7, that is, exactly those lanthanide dichlorides that (except PmCl₂) not only were successfully synthesized but also were the subject of some physicochemical measurements that required heating to high temperatures. For instance, saturated vapor pressure of

neodymium dichloride was measured by Kudin et al. (1993b), although the congruent character of its vaporization (or sublimation!) is doubtful. The enthalpies of sublimation of erbium and holmium dichlorides are smaller, which should cause a decrease in their stability. Indeed, attempts (Goryushkin et al., 1989c, 1990a, 1992a) to synthesize HoCl₂ did not result in its isolation in the pure form, although it was found that the compound had a structure similar to that of dysprosium, thulium, and ytterbium dichlorides. The obtained product melted incongruently at high temperatures with the appearance of holmium metal. Attempts at synthesizing erbium dichloride have been unsuccessful thus far.

As expected, such a kind of correlations are typical of other series of similar lanthanide compounds.

We performed a complete and consistent description of the thermodynamic properties of lanthanide trifluorides, trichlorides, and dichlorides. The thermodynamic functions for the condensed (up to 2000 K) and gaseous (up to 3000 K) states presented in a compact form can be included into the corresponding databases or separate programs for performing the necessary thermodynamic computations for the substances under consideration. We believe that, in spite of several approximations, the thermodynamic functions calculated by us are more reliable than those presented in Barin's reference work (Barin, 1995). This arises from the wide range of experimental data processed, for which close convergence of the $\Delta_{sub}H^{\circ}(298, III law)$ and $\Delta_{sub}H^{\circ}(298, II law)$ values was obtained. Analysis of both the enthalpies of atomization and the enthalpies of sublimation shows that the data obtained are in satisfactory agreement with the values found by independent methods.

The linear dependence of the characteristic parameters of the quasiharmonic approximation on the molar volume established by Chervonnyi and Chervonnaya (2007a,b) for compounds with the same crystal lattice type, which changes stepwise into another linear dependence when the type of the crystal lattice changes, was applied to calculation of the thermodynamic functions for lanthanum and lanthanide dichlorides. Its successful use for this class of compounds is fully proved. Obviously, this dependence can be used in processing the experimental data on other classes of lanthanide compounds. We believe that the know-how acquired during the calculation and estimation of the corresponding thermophysical parameters for RF₃, RCl₃ and RCl₂ compounds can be smoothly transferred to other classes of similar lanthanide compounds.

APPENDIX

Tables of polynomial coefficients for calculation of the reduced Gibbs energy for $R_m X_n$ (R = La–Lu; X = F, Cl; m = 1, n = 1-3; m = 2; n = 6)

	$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol}\cdot\text{K}), x = T \times 10^{-4}$								
RCl ₃	<i>f</i> ₁	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇		
LaCl ₃	567.82632	82.83643	-0.00197	0.66826	2.29476	-4.04377	3.58150		
CeCl ₃	548.71748	71.73476	0.00008	0.26696	142.53777	-270.96270	236.65714		
PrCl ₃	558.54567	73.88635	0.00007	0.27246	105.20572	-132.44615	77.78657		
NdCl ₃	562.74551	75.91576	-0.00077	0.35224	108.24794	-174.04689	131.27848		
PmCl ₃	573.16285	80.66147	-0.00280	0.65023	79.81605	-127.87181	93.59139		
SmCl ₃	587.47765	87.28807	-0.00443	0.95926	33.61159	-33.68892	6.05556		
EuCl ₃	580.91282	86.55798	-0.00102	0.62183	75.12492	-168.23388	146.91057		
GdCl ₃	581.69443	82.76748	-0.00217	0.70506	2.80732	-4.94491	4.37832		
TbCl ₃	553.94745	71.95303	0.00036	0.23109	124.93967	-189.6422	133.92577		
DyCl ₃	586.67046	82.37580	-0.00155	0.60498	-8.89726	83.32699	-96.98949		
HoCl ₃	593.20548	84.87002	-0.00225	0.66773	-26.47259	80.78700	-78.02894		
ErCl ₃	591.08996	84.56029	-0.00238	0.66836	-17.88787	44.97372	-36.86388		
TmCl ₃	590.59570	85.07880	-0.00246	0.66793	-25.25255	66.02677	-55.31039		
YbCl ₃	580.09034	82.96006	-0.00179	0.61849	1.44593	-2.62197	2.36369		
LuCl ₃	561.91217	82.70947	-0.00232	0.73294	3.23817	-5.70197	5.04747		

TABLE A1 Polynomial coefficients for calculation of the reduced Gibbs energy for RCl3(g); T = 298.15-3000 K

	$-[G^{\circ}(T) - H^{\circ}($	$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol} \cdot K), x = T \times 10^{-4}$							
RF ₃	f_1	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇		
LaF ₃	525.30155	81.27619	-0.00426	0.98982	13.80530	-24.17603	21.31785		
CeF ₃	507.18181	70.41355	-0.00125	0.47622	146.40886	-268.31719	228.69814		
PrF ₃	518.21082	73.5223	-0.00203	0.56086	112.98136	-154.21216	101.42992		
NdF ₃	511.86041	71.38189	-0.00155	0.53429	143.48556	-227.51353	169.59153		
PmF ₃	524.54573	76.94464	-0.00445	0.86458	108.21033	-174.81616	132.59119		
SmF_3	545.32048	85.92635	-0.00658	1.26186	42.10171	-47.76682	18.19272		
EuF ₃	534.23646	83.31466	-0.00278	0.87198	95.85673	-199.42860	171.07242		
GdF ₃	537.63550	80.82394	-0.00465	1.03998	17.11574	-29.93497	26.37201		
TbF ₃	511.16774	70.80594	-0.00174	0.49524	138.70703	-222.57802	168.02543		
DyF ₃	542.02634	80.45083	-0.00345	0.84093	7.28566	55.32129	-73.85474		
HoF ₃	548.39323	82.80802	-0.00486	1.03200	-11.24830	53.93092	-54.17242		
ErF ₃	545.71063	82.35791	-0.00499	1.01065	-1.70116	16.74788	-12.05012		
TmF ₃	545.63394	83.08410	-0.00402	0.86976	-11.42073	44.26166	-37.70948		
YbF ₃	535.63116	81.31623	-0.00416	0.94757	13.79482	-24.43609	21.69882		
LuF_3	515.35770	80.29472	-0.00503	1.08605	20.97697	-36.63697	32.24439		

TABLE A2 Polynomial coefficients for calculation of the reduced Gibbs energy for $RF_3(g)$; T = 298.15-3000 K

	$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol}\cdot\text{K}), x = T \times 10^{-4}$							
RCl ₂	f_1	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇	
LaCl ₂	478.04672	61.74076	-0.00441	0.69906	35.78734	-112.12300	137.13762	
CeCl ₂	441.69500	45.35325	0.00156	-0.12919	168.94769	-229.99666	139.10307	
PrCl ₂	469.61953	55.89060	-0.00160	0.28949	90.07683	-175.10221	148.78335	
NdCl ₂	476.88488	58.88409	-0.00226	0.44139	69.21803	-132.13247	105.55555	
PmCl ₂	482.18723	61.73744	-0.00219	0.53033	50.61237	-75.85304	39.29014	
SmCl ₂	487.50967	64.97770	-0.00103	0.40524	52.08330	-155.34332	157.00141	
EuCl ₂	478.12406	58.07327	-0.00103	0.36233	0.95281	-1.68038	1.48913	
GdCl ₂	497.26254	64.84296	-0.00152	0.47994	14.02198	-51.39373	56.71585	
TbCl ₂	479.42091	56.27177	-0.00021	0.22224	4.31073	76.76783	-96.53824	
DyCl ₂	487.16819	58.91793	-0.00069	0.27419	-19.91997	84.35308	-94.42136	
HoCl ₂	490.29063	60.46530	-0.00135	0.35002	-29.32485	79.14706	-71.09111	
ErCl ₂	489.38531	60.77284	-0.00138	0.34153	-34.41203	96.11413	-90.92267	
TmCl ₂	478.42376	58.57431	-0.00081	0.29081	-3.29640	4.50330	3.40886	
YbCl ₂	459.78099	58.05395	-0.00110	0.37490	1.09675	-1.93380	1.71345	
LuCl ₂	484.53176	64.72786	-0.00282	0.62685	-77.84564	193.97723	-165.43120	

TABLE A3 Polynomial coefficients for calculation of the reduced Gibbs energy for RCl2(g); T = 298.15-3000 K

	$-[G^{\circ}(T) - H^{\circ}(T)]$	$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol}\cdot K), x = T \times 10^{-4}$							
RF ₂	<i>f</i> ₁	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇		
LaF_2	450.81674	61.14119	-0.00569	0.89690	40.23129	-119.92048	144.02272		
CeF ₂	417.22083	45.86178	0.00047	0.03218	167.16710	-228.34488	136.23989		
PrF ₂	446.21522	56.81929	-0.00289	0.53517	83.17726	-164.59575	140.86072		
NdF ₂	451.08332	58.73778	-0.00351	0.62971	69.10987	-131.63435	105.22611		
PmF ₂	455.05615	61.03364	-0.00324	0.69131	54.48420	-81.88750	44.34891		
SmF_2	460.02411	64.24905	-0.00241	0.60845	57.47670	-164.79802	165.34438		
EuF_2	450.57270	57.32238	-0.00242	0.56629	6.50964	-11.42009	10.08268		
GdF_2	469.65875	64.07180	-0.00293	0.68454	19.72765	-61.39296	65.53751		
TbF ₂	451.37256	55.47567	-0.00113	0.33430	12.99144	60.28021	-82.63001		
DyF ₂	459.61534	58.18575	-0.00214	0.49861	-14.54862	74.76827	-85.75833		
HoF ₂	462.44379	59.63988	-0.00280	0.55377	-23.22755	68.49249	-61.71368		
ErF_2	461.82937	60.29148	-0.00198	0.42790	-32.81129	99.10898	-96.55287		
TmF_2	451.53807	58.21491	-0.00196	0.47046	-0.52465	-0.43200	7.89061		
YbF ₂	431.68837	57.19958	-0.00256	0.58124	7.41289	-12.99666	11.46958		
LuF_2	456.32940	63.86689	-0.00428	0.83323	-71.48169	182.83232	-155.60401		

TABLE A4 Polynomial coefficients for calculation of the reduced Gibbs energy for $RF_2(g)$; T = 298.15-3000 K

		$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol} \cdot K), x = T \times 10^{-4}$						
RF ₃	Т (К)	f ₁	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇
LaF ₃	298.15–1766	336.52239	94.98865	-0.00407	1.50174	79.10312	-21.10476	99.83309
	1766-2000	439.26822	153.33000	0	3.64588	0	0	0
CeF ₃	298.15-1703	339.27726	91.67719	-0.00299	1.28305	120.20567	-10.39777	-50.20489
	1703-2000	459.96946	154.46000	0	3.03094	0	0	0
PrF ₃	298.15-1670	350.91926	94.73400	-0.00336	1.33504	69.04847	183.02256	-304.27584
	1670-2000	466.37591	155.93000	0	2.86601	0	0	0
NdF ₃	298.15-1649	344.66414	93.27971	-0.00351	1.38165	108.03711	61.94686	-167.57336
	1649-2000	464.42080	154.03000	0	2.76015	0	0	0
PmF ₃	298.15-1605	321.14844	86.39373	-0.00326	1.35403	223.07683	-302.27391	369.77436
	1605-2000	463.60877	152.34000	0	2.57467	0	0	0
SmF ₃	298.15-743	222.84439	60.98107	-0.00215	0.89623	890.07367	-3916.89267	10,067.24714
	743–1571	346.86195	96.91147	-0.00652	1.57182	137.95287	-105.12129	135.62677
	1571-2000	464.40820	151.26000	0	1.94665	0	0	0
EuF_3	298.15-973	345.77784	99.58562	-0.00419	1.61299	167.80167	-414.98538	1060.80427
	973-1549	325.07531	87.81385	0.000755	0.15478	251.48945	-399.32619	462.19557
	1549-2000	467.68213	148.45000	0	0.40291	0	0	0
GdF ₃	298.15-1347	336.92563	92.36009	-0.00444	1.56299	114.62710	-133.81196	268.75330
	1347-1501	339.16305	91.19642	-0.00338	0.87028	115.93265	-102.13216	171.76916
	1501-2000	446.34054	137.90000	0	0.40879	0	0	0
TbF ₃	298.15-1446	338.38601	91.85706	-0.00363	1.35193	107.54282	79.25802	-234.18639
-	1446-2000	458.78569	141.73000	0	0.24866	0	0	0

 TABLE A5
 Polynomial coefficients for calculation of the reduced Gibbs energy for RF₃ (cr, liq)

TABLE A5	(continued)
	continucu

		$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol}\cdot\text{K}), x = T \times 10^{-4}$							
RF ₃	<i>Т</i> (К)	f ₁	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇	
DyF ₃	298.15-1426	353.02523	96.32317	-0.00441	1.54007	49.62900	117.67717	-90.73585	
-	1426-2000	453.32488	137.30000	0	-0.09962	0	0	0	
HoF ₃	298.15-1416	341.09078	92.54749	-0.00439	1.51688	109.89057	-119.25231	280.27592	
	1416-2000	446.87718	132.71000	0	-0.39926	0	0	0	
ErF ₃	298.15-1388	335.98586	91.30598	-0.00428	1.46345	129.01016	-183.23248	358.90116	
	1388-1413	357.75088	89.71740	0	-1.78304	97.99313	0	0	
	1413-2000	443.31463	129.85000	0	-0.81979	0	0	0	
TmF ₃	298.15-1325	339.59938	93.33144	-0.00364	1.37581	103.80873	-114.80422	281.67631	
	1325-1431	356.01805	89.39863	0	-2.00761	100.78897	0	0	
	1431-2000	441.98893	128.51000	0	-1.36472	0	0	0	
YbF ₃	298.15-1267	334.75403	93.46885	-0.00434	1.53179	108.82279	-138.06449	298.89560	
	1267-1435	364.43368	91.96578	0	-1.85128	45.98289	0	0	
	1435-2000	429.72760	125.29000	0	-0.99019	0	0	0	
LuF ₃	298.15-1230	305.30823	89.32943	-0.00455	1.56459	161.13905	-306.20291	595.25111	
	1230-1455	335.57689	91.14773	0	-1.11109	91.78690	0	0	
	1455–2000	412.62635	123.73000	0	-1.24048	0	0	0	

		–[G°(T) − H	°(0)]/ $T = f_1 + f_2$	$f_2 \ln x + f_3 x^{-2} + f_3 x^{-2}$	$-f_4x^{-1} + f_5x +$	$f_6 x^2 + f_7 x^3$, J/(mo	ol·K), $x = T \times 10^{-4}$	- 4			
RCl_3	Т (К)	<i>f</i> ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇			
LaCl ₃	298.15-1135	399.91900	104.32434	-0.00254	1.22921	-79.68743	806.76307	-1280.46527			
	1135-2000	499.68469	142.50000	0	-0.74775	0	0	0			
CeCl ₃	298.15-1090	426.56864	107.63713	-0.00258	1.23300	-182.47170	1508.34671	-3001.05884			
	1090-2000	523.13388	146.27000	0	-0.62127	0	0	0			
PrCl ₃	298.15-1061	427.40897	107.14015	-0.00242	1.18395	-170.06277	1450.38400	-2801.72427			
	1061-2000	525.52436	146.78000	0	-0.35084	0	0	0			
NdCl ₃	298.15-1032	419.38405	104.77243	-0.00194	1.08329	-122.57431	1334.61882	-2779.01327			
	1032-2000	524.83432	146.89000	0	-0.10035	0	0	0			
PmCl ₃	298.15-994	399.42124	99.52635	-0.00206	1.06396	-3.47687	873.58656	-1950.48263			
	994-2000	527.72319	147.26000	0	-0.12306	0	0	0			
$SmCl_3$	298.15-950	380.14039	95.77893	-0.00231	1.09673	131.55907	228.51473	-522.38217			
	950-2000	531.00050	148.30000	0	-0.17390	0	0	0			
EuCl ₃	298.15-894	451.57948	119.94781	-0.00316	1.50380	-228.64973	1670.80880	-3614.19683			
	894-2000	533.67284	150.00000	0	-0.24790	0	0	0			
GdCl ₃	298.15-873	428.52776	108.58301	-0.00308	1.36501	-175.68260	1336.76947	-2737.97721			
	873-2000	512.16694	139.26000	0	-0.05020	0	0	0			
TbCl ₃	298.15-783	439.83864	110.52220	-0.00299	1.29706	-245.05894	1843.92363	- 3893.56949			
	783-855	467.06745	123.90000	0	1.03137	0	0	0			
	855-2000	516.75448	142.44000	0	0.68142	0	0	0			
DyCl ₃	298.15-611	363.11502	86.38161	-0.00117	0.79269	483.45986	-3430.93448	14,569.33184			
-	611–909	412.43288	98.15489	-0.00264	0.83929	35.37167	301.32282	-38.26303			
	909–2000	516.78753	144.77000	0	2.00149	0	0	0			

TABLE A6 Polynomial coefficients for calculation of the reduced Gibbs energy for RCl₃(cr, liq)

TABLE A6	(continued)	

		–[G°(T) − H	$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol}\cdot\text{K}), x = T \times 10^{-4}$						
RCl ₃	Т (К)	<i>f</i> ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇	
HoCl ₃	298.15-993	454.18061	111.05296	-0.00232	1.15873	-226.72234	1468.84029	- 2699.01551	
	993-2000	515.48085	143.47000	0	1.42307	0	0	0	
ErCl ₃	298.15-1046	445.92768	109.03160	-0.00224	1.12116	-182.43065	1256.04848	-2214.41738	
	1046-2000	516.19920	142.70000	0	0.87645	0	0	0	
TmCl ₃	298.15-1092	437.77156	107.28652	-0.00204	1.06645	-145.94596	1079.70350	-1787.66520	
	1092-2000	510.53338	142.32000	0	0.98574	0	0	0	
YbCl ₃	298.15-1127	433.56710	107.66352	-0.00211	1.12467	-143.28389	1048.20254	-1709.47619	
	1127-2000	503.54626	141.50000	0	0.94875	0	0	0	
LuCl ₃	298.15-1198	404.34532	104.01434	-0.00221	1.15110	-78.05031	769.30240	-1108.37872	
	1198–2000	485.63507	141.01000	0	0.77300	0	0	0	

		$-[G^{\circ}(T) - H^{\circ}($	$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol}\cdot K), x = T \times 10^{-4}$								
R ₂ Cl ₆	Т (К)	f ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇			
La ₂ Cl ₆	298.15-1500	1028.65892	181.03007	-0.00413	1.57490	21.16065	- 58.90959	85.93730			
	1500-3000	1033.81723	182.90054	-0.00489	1.65808	0.06144	-0.05911	0.03091			
Ce_2Cl_6	298.15-1500	999.28471	161.63360	0.0000037172	0.81925	241.30844	-330.34560	26.05265			
	1500-3000	1133.61213	223.1575	-0.06744	5.48317	-127.24202	106.77096	-49.82483			
Pr_2Cl_6	298.15-1500	1017.70038	166.60664	-0.00082	0.91401	178.76126	-158.45109	-24.40832			
	1500-3000	1036.76500	177.90480	-0.02859	2.23203	145.74140	-188.56760	108.20631			
Nd_2Cl_6	298.15-1500	989.43288	158.72678	0.0003	0.65939	337.89016	-700.38083	775.19759			
	1500-3000	1083.03314	199.45858	-0.04777	3.65632	32.91805	-77.62704	53.27544			
Pm_2Cl_6	298.15-1500	988.47692	161.49649	-0.00238	1.04170	374.48872	-912.76976	1199.40133			
	1500-3000	1073.25912	195.34363	-0.03383	3.14776	57.03899	-102.55614	65.88717			
Sm_2Cl_6	298.15-1500	1020.64738	176.42547	-0.00628	1.74478	265.82388	-693.25133	1005.17748			
	1500-3000	1026.23528	173.57328	0.00995	0.89597	174.57512	-222.55918	126.50531			
Eu_2Cl_6	298.15-1500	1063.34068	194.26738	-0.00373	1.74358	85.36620	-121.22047	-60.97402			
	1500-3000	1171.55564	247.73177	-0.0846	6.49779	-186.79957	142.65648	-60.66425			
Gd_2Cl_6	298.15-1500	1044.91470	180.38165	-0.00472	1.70298	28.50275	-79.60885	116.58404			
	1500-3000	1051.85040	182.89471	-0.00573	1.81456	0.08315	-0.07999	0.04183			
Tb ₂ Cl ₆	298.15-1500	1024.33346	170.87017	-0.00248	1.18844	111.87987	50.77755	-405.2866			
	1500-3000	1096.47724	211.63875	-0.08652	5.56229	-20.93331	-27.95232	30.04863			
Dy_2Cl_6	298.15-1500	1072.27281	186.25810	-0.00525	1.76523	-77.12403	332.49372	-424.16920			
	1500-3000	964.89375	136.25904	0.06659	-2.39870	237.76017	-192.61556	71.80330			
Ho ₂ Cl ₆	298.15-1500	1057.61798	182.21638	-0.00453	1.57776	4.48135	-25.28084	149.51162			
	1500-3000	1000.06901	152.65911	0.04528	-1.21599	138.1304	-104.56524	37.65116			

TABLE A7 Polynomial coefficients for calculation of the reduced Gibbs energy for R₂Cl₆(g)

TABLE A7	(continued)

		$-[G^{\circ}(T) - H^{\circ}($	$[0]/T = f_1 + f_2$	$\ln x + f_3 x^{-2} + f_4 x^{-2}$	$x^{-1} + f_5 x + f_6 x^2$	$+ f_7 x^3$, J/(mol·K)	$x = T \times 10^{-4}$	
R ₂ Cl ₆	Т (К)	<i>f</i> ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇
Er ₂ Cl ₆	298.15-1500	1048.00809	180.05205	-0.00434	1.52413	36.48841	-124.87325	247.90877
	1500-3000	1020.70563	163.19026	0.03668	-0.48408	75.36432	-42.18680	6.91165
Tm ₂ Cl ₆	298.15-1500	1042.38585	180.06712	-0.00435	1.50370	35.43175	-125.80822	279.33707
	1500-3000	1004.85875	157.56785	0.04833	-1.10089	95.30161	-44.57427	0.00370
Yb_2Cl_6	298.15-1500	1034.90918	181.00722	-0.00437	1.61000	21.95452	-61.98928	91.24448
	1500-3000	1040.21985	182.91700	-0.00509	1.69251	0.00534	-0.00816	0.00532
Lu ₂ Cl ₆	298.15-1500	995.32101	179.66761	-0.00528	1.81634	36.48382	-101.80789	148.99382
	1500-3000	1004.20434	182.88794	-0.00659	1.95955	0.10839	-0.10426	0.05452

		–[G°(T) − H	\circ (0)]/ $T = f_1 + i$	$f_2 \ln x + f_3 x^{-2} + $	$f_4 x^{-1} + f_5 x + t$	$f_6 x^2 + f_7 x^3$, J/(mo	ol·K), $x=T imes 10^-$	- 4
RCl ₂	Т (К)	f ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇
LaCl ₂	298.15-1070	285.26927	67.71060	-0.000885	0.62513	159.65492	141.02494	-771.29689
	1070-2000	412.76107	113.60000	0	-0.15140	0	0	0
CeCl ₂	298.15-1080	308.26252	72.72540	-0.00117	0.66555	60.90154	546.62682	-1204.72755
	1080-2000	425.77241	118.20000	0	0.12930	0	0	0
PrCl ₂	298.15-1090	289.94769	67.68104	-0.000715	0.53829	188.05954	-37.28034	-202.68066
	1090-2000	420.96003	114.40000	0	-0.30440	0	0	0
NdCl ₂	298.15-1098	285.31128	67.26881	-0.00115	0.62161	234.20161	-284.98548	366.67137
	1098-2000	421.58123	114.90000	0	-0.29838	0	0	0
PmCl ₂	298.15-1110	293.87490	71.71837	-0.00190	0.80944	210.59265	-269.68725	463.63130
	1110-2000	422.14303	116.20000	0	-0.29550	0	0	0
$SmCl_2$	298.15-1043	331.37045	84.88824	-0.00169	0.92434	26.28127	436.96817	-1053.45191
	1043-1132	415.55889	128.20000	0	2.99586	0	0	0
	1132-2000	421.90995	115.60000	0	-0.83048	0	0	0
EuCl ₂	298.15-1020	314.48278	76.02992	-0.00184	0.86663	24.94651	346.12021	-656.23270
	1020-1127	397.53290	118.80000	0	2.89200	0	0	0
	1127-2000	402.56173	105.80000	0	-0.87314	0	0	0
GdCl ₂	298.15-1143	341.48740	83.73746	-0.00184	0.92871	5.28873	459.67650	-963.32980
	1143-2000	425.29310	113.40000	0	-0.72164	0	0	0
TbCl ₂	298.15-1113	339.69920	79.66212	-0.00181	0.82327	-49.15311	661.34280	-1108.39900
	1113–2000	416.16070	110.90000	0	0.06303	0	0	0

 TABLE A8
 Polynomial coefficients for calculation of the reduced Gibbs energy for RCl₂(cr, liq)

TABLE A8	(continued)	

		–[G°(T) – H	$[\circ(0)]/T = f_1 + f_2$	$f_2 \ln x + f_3 x^{-2} + $	$f_4 x^{-1} + f_5 x + f_5 x$	$f_6 x^2 + f_7 x^3$, J/(mo	ol·K), $x = T imes 10^{-1}$	10 ⁻⁴				
RCl ₂	Т (К)	<i>f</i> ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇				
DyCl ₂	298.15-1086	337.79530	77.66255	-0.00126	0.68447	2.49315	395.41710	-564.26560				
HoCl ₂	298.15–1059	420.39740 335.30010	77.15423	-0.00126	0.67065	7.53982	360.03610	-551.91110				
ErCl ₂	1059–2000 298.15–1031	417.22810 314.93980	72.05117	0 	-0.07395 0.55956	0 128.2088	0 - 259.30210	0 715.69860				
TmCl ₂	1031–2000 298.15–991	413.48390 331.56465	108.00000 78.18438	0 -0.00130	-0.02854 0.71441	0 	0 445.44015	0 785.36220				
YbCl ₂	991–2000 298.15–987	409.32566 309.73153	107.30000 76.82669	0 - 0.00154	-0.07677 0.78342	0 10.97569	0 365.22281	0 -628.40511				
- LuCla	987–2000 298 15–949	390.86294 312 76810	106.50000 76.23473	0 0.00153	-0.05935 0.77947	0 25.67889	0 280 32850	0 374 67140				
LuCl2	949–2000	396.79970	106.40000	0	-0.02937	0	0	0				

TABLE A9 Polynomial coefficients for calculation of the reduced Gibbs energy for LaF(g) and LaCl(g), approximation of the reduced Gibbs energy calculated from statistical sums obtained by direct summation

		$-[G^{\circ}(T) - H^{\circ}(C)]$	$-[G^{\circ}(T) - H^{\circ}(0)]/T = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol} \cdot K), x = T \times 10^{-4}$							
_	Т (К)	<i>f</i> ₁	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇		
LaF	298.15–1000	-624.76095	-248.28896	0.02850	-6.44818	5467.90751	-22,131.41968	44,200.49996		
	1000–3000	302.70505	9.91066	0.10826	-4.78750	133.21891	-122.42423	56.59831		
LaCl	298.15–1000	790.20952	194.83037	-0.03251	5.73311	- 1536.16355	3115.49452	- 1796.82163		
	1000–3000	298.19341	4.62787	0.06387	-3.98976	194.22441	215.38107	121.40538		

	$-[G^{\circ}(T) - H^{\circ}($	$[0)]/T = f_1 + f_2 \ln t$	$x + f_3 x^{-2} + f_4 x^{-1}$	$+f_5x+f_6x^2+f_7$	x^3 , J/(mol·K), $x = T$	$\times 0^{-4}$	
RF	f_1	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇
CeF	341.08078	40.78094	-0.00828	0.95099	164.88205	-334.1073	297.38651
PrF	345.09816	35.52003	-0.00044	0.16101	60.99619	-1.09992	-63.49421
NdF	354.37643	40.18604	-0.00218	0.41072	49.25396	-40.36876	2.19879
PmF	353.85092	41.72604	-0.00282	0.48948	70.85560	-148.36236	127.85775
SmF	357.28278	44.64247	-0.00344	0.55029	75.60396	-204.1143	209.79207
EuF	342.09845	35.21000	-0.00205	0.29859	58.89935	-127.11622	125.07491
GdF	356.59811	38.61414	0.00031	0.12701	36.13894	-15.1087	-27.30752
TbF	321.06903	25.31859	0.00215	-0.18401	132.96119	-107.16683	-9.11369
DyF	381.07635	46.73273	-0.00366	0.65947	-69.54572	161.35266	-150.87369
HoF	379.44824	45.61303	-0.00271	0.55159	-65.8932	139.34697	-119.55412
ErF	369.87780	41.86422	-0.00142	0.35219	-44.44635	114.02612	-106.79664
TmF	353.31703	37.06641	-0.00108	0.21489	4.01780	-5.07402	11.80427
YbF	338.02531	36.8209	-0.00131	0.26343	6.73168	-7.62712	6.79035
LuF	328.58085	36.24540	-0.00166	0.29048	10.49374	-14.92209	13.14678

TABLE A10 Polynomial coefficients for calculation of the reduced Gibbs energy for RF(g) (the electronic contribution was found from the excitation energies of the free ions R^+ (Martin et al., 1978); T = 298.15-3000 K)

	$-[G^{\circ}(T) - H^{\circ}(C)]$	$D)]/T = f_1 + f_2 \ln x$	$x + f_3 x^{-2} + f_4 x^{-1}$	$+f_5x+f_6x^2+f_6x^2$	$_7x^3$, J/(mol·K), $x = T$	$\times 10^{-4}$	
RF	<i>f</i> ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇
CeF	410.57557	65.86339	-0.00682	1.37698	-143.14988	397.30358	-487.02680
PrF	401.22259	65.18231	-0.01016	1.63217	-69.44416	195.48265	-262.04809
NdF	265.09319	5.16934	0.01236	-1.40701	312.72252	-268.97679	-30.76885
PmF	392.68429	56.5502	-0.00498	0.8831	-39.46183	-633.87989	4700.51062
	1151.66634	462.38531	-0.71179	41.25006	-1813.0066	1929.40508	-1082.59801
SmF	346.96992	41.53085	-0.00332	0.50738	60.28896	-117.03375	99.64239
EuF	352.68193	39.17548	-0.00315	0.46315	26.30361	-72.02420	77.40080
GdF	348.52695	35.63403	0.00058	0.09407	-54.46094	393.40343	-537.38051
TbF	491.18025	87.85052	-0.00941	1.79458	-571.89425	952.65991	4251.01177
	2199.2949	964.99954	-1.32121	82.44023	-4591.6501	5558.71027	-3516.11568
DyF	418.51267	66.66709	-0.00753	1.34589	-176.51046	- 399.92269	5797.2491
	1785.61159	767.80169	-1.08226	66.31610	-3494.18372	4120.58526	-2549.34863
HoF	412.18855	57.53226	-0.00143	0.51183	-240.1209	632.39726	-578.60049
ErF	373.22067	44.8431	-0.00268	0.44873	-78.00022	184.13476	-113.42381
TmF	360.79141	42.97691	-0.00304	0.45481	-6.22272	33.97406	-35.17002
YbF	349.79569	40.62851	-0.00194	0.37802	-49.52408	164.97327	-167.89746

TABLE A11 Polynomial coefficients for calculation of the reduced Gibbs energy for RF(g) (the electronic contribution was found from the excitation energies of RF (Kaledin et al., 1996a, 1998); T = 298.15-3000 K)^a

^a Data on PmF, TbF, and DyF were approximated separately in two temperature ranges: 298.15–1000 K (first line) and 1000–3000 K (second line).

	$\frac{-[G^{\circ}(T) - H^{\circ}(0)]}{T} = f_1 + f_2 \ln x + f_3 x^{-2} + f_4 x^{-1} + f_5 x + f_6 x^2 + f_7 x^3, J/(\text{mol}\cdot K), x = T \times 10^{-4}$						
RCl	<i>f</i> ₁	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇
CeCl	356.46274	41.60161	-0.00745	0.86354	159.29217	-323.60567	288.16753
PrCl	360.56224	36.36900	0.00040	0.07365	55.21155	9.75607	-73.02252
NdCl	369.91692	41.06171	-0.00133	0.32335	43.30091	-29.17855	-7.62130
PmCl	369.46432	42.62561	-0.00197	0.40215	64.73262	-136.87313	117.77688
SmCl	372.95851	45.56461	-0.00258	0.46292	69.34204	-192.34317	199.46511
EuCl	356.72938	35.67970	-0.00132	0.20711	56.05815	-121.03396	119.73429
GdCl	372.37993	39.5735	0.00118	0.03955	29.62911	-2.87247	-38.04000
TbCl	336.90340	26.29332	0.00302	-0.27163	126.36506	-94.73842	-20.01357
DyCl	396.95023	47.72018	-0.00277	0.57168	-76.22296	173.94026	-161.91223
HoCl	395.36157	46.60996	-0.00183	0.46359	-72.61419	152.05325	-130.69596
ErCl	385.82208	42.86875	-0.00053	0.26387	-51.20335	126.82807	-118.02165
TmCl	369.28641	38.07517	-0.00019	0.12619	-2.75781	7.78187	0.53260
YbCl	352.86096	37.33827	-0.00054	0.16915	3.66895	-0.93300	0.91721
LuCl	344.58401	37.25481	-0.00076	0.20093	3.74944	-2.05562	1.86637

TABLE A12 Polynomial coefficients for calculation of the reduced Gibbs energy for RCl(g) (the electronic contribution was found from the excitation energies of the free ions R^+ (Martin et al., 1978); T = 298.15-3000 K)

	$-[G^{\circ}(T) - H^{\circ}(C)]$	$D)]/T = f_1 + f_2 \ln x$	$+f_3x^{-2}+f_4x^{-1}$	$+f_5x+f_6x^2+f_5x^2$	$T_7 x^3$, J/(mol·K), $x = T$	× 10 ⁻⁴	
RCl	f ₁	f ₂	f ₃	f ₄	<i>f</i> ₅	f ₆	f ₇
CeCl	382.33004	46.44261	0.00459	0.01889	-0.71389	124.91299	-226.00673
PrCl	363.41650	36.28049	0.00522	-0.41482	32.47244	143.69118	-272.14390
NdCl	366.72107	37.23226	0.00410	-0.25083	1.76543	285.98370	-456.66632
PmCl	230.26335	-11.23593	0.01999	-2.35268	499.64824	-641.20540	308.79946
SmCl	299.60685	15.68276	0.01022	-1.05599	221.48599	-134.53563	-124.75369
EuCl	356.58868	35.62189	-0.00129	0.20409	56.39974	-120.57927	116.33465
GdCl	324.34321	23.44373	0.00372	-0.40166	115.21548	4.36555	-157.99865
TbCl	578.92153	108.54129	-0.00954	2.03185	-978.56170	2579.16680	1207.05740
	2369.71789	1040.08008	-1.42290	88.75867	-4994.21303	6062.11769	-3839.83508
DyCl	404.23224	51.04062	-0.00236	0.43769	-9.11100	-834.60754	4653.90481
	485.22979	141.79434	-0.37024	16.62206	31.49877	-544.59096	603.14064
HoCl	372.99046	39.66716	-0.00073	0.07225	-16.00601	178.95422	-205.50672
ErCl	391.25894	45.96249	-0.00240	0.39582	-95.79273	235.82921	-160.11306
TmCl	404.98612	51.57916	-0.00114	0.39726	-102.54341	209.58840	-187.76213
YbCl	353.06152	37.44971	-0.00062	0.17725	4.00921	-8.29244	23.31731

TABLE A13 Polynomial coefficients for calculation of the reduced Gibbs energy for RCl(g) (the electronic contribution was found from the excitation energies of RCl (Kaledin et al., 1996a; T = 298.15-3000 K)^a

^a Data on TbCl and DyCl were approximated separately in two temperature ranges: 298.15–1000 K (first line) and 1000–3000 K (second line).

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