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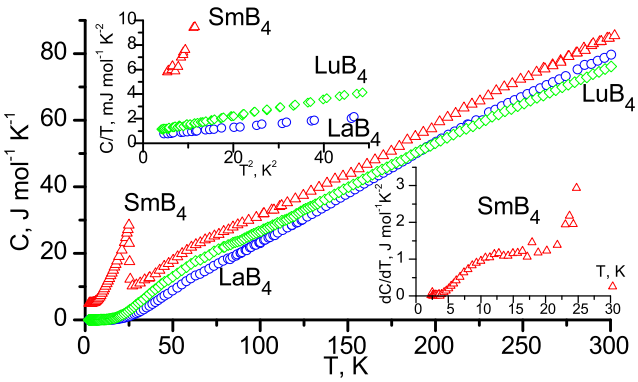

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Peculiarities of Electronic, Phonon and Magnon Subsystems of Lanthanum and Samarium Tetraborides

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Keywords: rare earth alloys and compounds; heat capacity; phonons; thermal expansion; thermal analysis.

Experimental research was carried out to study the temperature dependences of heat capacity C_p(T = 2–300 K), lattice parameters *a(T),* and *c(T),* (5–300 K) of lanthanum and samarium tetraborides. A comparison with data obtained previously for LuB_4 reveals the peculiar influence of lanthanide contraction and the rare-earths mass on the thermodynamic properties of rare earth tetraborides at low and high temperatures. Sharp anomalies were found in the heat capacity and thermal expansion for SmB_4 at T_N = 25.1 K, conditioned by the phase transition into antiferromagnetic state. The more poorly defined heat capacity anomaly around 7 K is referred to the quadrupole orbital fluctuation of the atomic magnetic moments for Sm^{3+} ions. The electronic, lattice, and magnetic contributions to the heat capacity and thermal expansion of samarium tetraboride were defined. Our approach makes it possible to adequately approximate the lattice components of heat capacity and thermal expansion by combining the Debye and Einstein contributions, which are based on the joint analysis of calorimetric and X-ray data. The influence of the frustration of the atomic magnetic moment system for Sm^{3+} ions on the thermodynamic characteristics of the samarium tetraboride magnetic phase transition was revealed.

1. Intoduction

Tetraborides of rare earth elements (REEs), RB_4 (where ‘R’ represents a rare earth metal), present unusual magnetic, electronic and lattice properties. The metallic type of conductivity is characteristic to rare earth tetraborides [1, 2]. In the region of moderate temperatures, the majority of RB_4 compounds are paramagnetic. As the temperature is lowered, the tetraborides containing an R^{3+} ion pass to a

magnetically ordered state [3-7]. As a rule, this transition occurs to an antiferromagnetic state (however, PrB_4 transforms to a ferromagnetic state).

The peculiar crystalline structure of RB_4 compounds determines the mutual spatial arrangement in rare earth metals and boron sub-lattices, and also governs numerous interesting properties of rare earth tetraborides.

Rare earth tetraborides are crystallised into the tetragonal structure of UB_4 type [8]. Four formula units correspond to the elementary cell. Boron atoms make up B_6 octahedrons, rigidly bound to one another by boron atomic chains. These chains, together with the edges of the octahedrons, form heptagonal rings. Thus, the boron sublattice of the tetraborides possesses the structural elements typical of both hexaborides and diborides of rare earth elements.

The rare earth atoms make up squares and triangles and are positioned above the boron atomic rings. This arrangement leads to the formation of the Shastry-Sutherland Lattice (SSL) [9]. The phenomenon of geometrical frustration is characteristic of SSL, for which a completely ordered state of the substance's magnetic subsystem is not possible up to absolute zero temperature.

The electronic, magnetic, and thermodynamic properties of heavy rare earth element tetraborides have been the subject of numerous studies [1-7, 10-23]. However, fewer studies exist of the properties of light RE-tetraborides (beginning with LaB_4), at low temperatures. Previous works [24, 25] have shown that Nd (4.8, 7, and 17.2K), Pr (24K), and Sm (26K) tetraborides pass into a magnetically ordered state. At about 7 K, the second phase transition in samarium tetraboride occurs, which has been attributed to the frustration of the SmB_4 spin system [25]. This transition is also manifest on the temperature dependence of electrical resistance in the form of curve fracture of the derivative of electrical resistance.

This work is devoted to analysing the influence of tetraboride structure and the type of R^{3+} rare earth ion on crystalline lattice dynamics and the behaviour of lanthanum and samarium tetraboride electronic and magnetic subsystems. To these ends, we synthesised powder samples of LaB_4 and SmB_4, and experimentally defined the temperature dependencies of both their heat capacity (over 2 – 300 K) and lattice parameters (over 5 – 300 K).

II. Experiment

The synthesis of LaB_4 and SmB_4 samples was executed in two stages. First, the hexaborides of these REEs were obtained by the borothermal reduction from their oxides in a vacuum at $T \approx 1773$ K: $R_2O_3+15B=2RB_6+3BO\uparrow$.

Lanthanum tetraboride was obtained from the mixture of its hexaboride and metallic lanthanum by melting it in an electric arc surrounded by argon: $2LaB_6 + La = 3LaB_4$.

Samarium tetraboride was obtained from its hexaboride as a result of a similar reaction in the crucible from TiB_2 – TiC at 1573 K within 1.5 hr. After the first annealing, the sample was powdered, and after adding a small amount of metallic samarium was heated again under the same conditions. This procedure was repeated until all the blue samarium hexaboride had reacted.

The synthesised tetraboride samples had the following composition:

LaB_4: La – 75.8%, B – 24.8%, O_2 – 0.14%;

SmB_4: Sm – 76.7%, B – 22.9%, O_2 – 0.3%.

The spectral analysis of the RB_4 samples did not reveal the magnetic impurities, the presence of which could have significantly impaired the sample's characteristics, especially at low temperatures. Atomic absorption spectrometer MGA-915 was used (electro-thermal atomization and Zeeman correction), the manufacturer – the group of companies ''Lumex''. The boron content was determined in the graphite cell with zirconia covering, the detection limit of 20 ng. The content of rare earth was set on SF-56 spectrophotometer (producer – EDO ''Spectrum'') with Arsenazo III with accuracy higher than 1 mg/L.

The X-ray diffraction patterns of the synthesised samples corresponded to ASTM data. Reflexes of extraneous phases were not observed.

The heat capacity of lanthanum and samarium tetraboride samples over 2 – 300 K was measured using the absolute adiabatic method with periodic heating, using an automated calorimeter [18, 26]. The measurement error was 3% between 2 – 20 K; when the temperature increased to 60 K, the measurement error decreased to 1% and remained within these limits until 300 K. Measurements of the heat capacity of electrolytic copper melted in a vacuum confirmed these error values.

The thermal expansion of lanthanum and samarium tetraborides over 5 – 300 K was studied using an X-ray diffractometer and following the Debye-Scherrer powder method with an X-ray helium cryostat [19, 25]. The measurement of interplane distances in the tetraborides was undertaken to an accuracy of $\pm 2 \times 10^{-5}$ Å. For comparison, a small amount of silicon powder was added to the tetraboride sample under study.

3. Results and Discussion

The experimental temperature dependencies of heat capacity $C_p(T)$ of lanthanum and samarium tetraborides are shown in Fig. 1. The same figure presents the data $C_p(T)$ for LuB_4 [28].

The most important point is the mutual arrangement of $C_p(T)$ dependencies for diamagnetic LaB_4 and LuB_4. The heat capacity of these tetraborides, with the exception of its behaviour over the lowest temperatures, is determined by their phonon subsystem.

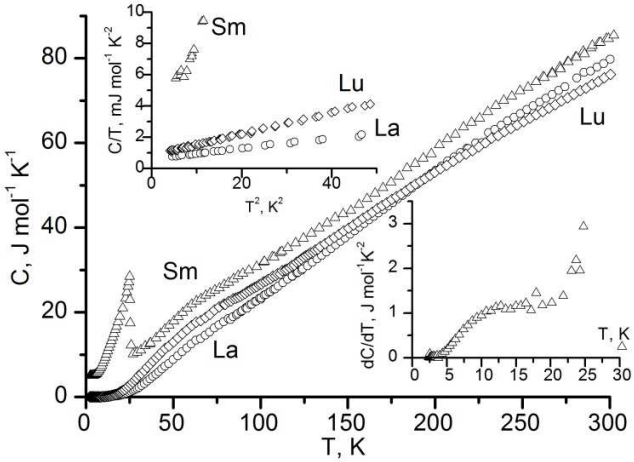

Fig. 1. The heat capacities of RE-tetraborides. LaB_4, SmB_4– present work, LuB_4 – [28]. The dependence for SmB_4 was shifted to higher values by 5 J mol^{-1} K^{-1} for more clarity. Lower insert: derivative of the samarium tetraboride heat capacity.

At low temperatures, the $C_p(T)$ dependence for rare earth tetraborides is determined by the vibrations of the rare earth metal sublattice. The larger mass of Lu^{3+} ions, as opposed to La^{3+}, corresponds to the lower oscillation frequency, and consequently to the lower characteristic temperature. This temperature corresponds to the larger heat capacity, as seen from the experimental results. The smaller values of the LuB_4 lattice parameters, relative to those of LaB_4 (lanthanide contraction), diminish the influence of the Lu^{3+} ions' larger mass on the oscillation frequency, but not to such an extent as to qualitatively change the correlation between the values of tetraboride heat capacity in the low-temperature region.

At higher temperatures, the thermodynamic properties of tetraborides greatly influence high-frequency oscillations in the boron sublattice. In this case, the principal influence on the oscillation frequency is the phenomenon of lanthanide contraction, mentioned above. The smaller values of the lutetium boride lattice parameters result in a higher frequency of boron sublattice oscillations, a higher characteristic temperature, and consequently a lower heat capacity (Fig. 1).

The presence of the Sm^{3+} paramagnetic ion in the structure of samarium tetraboride leads to anomalies in the temperature dependency, $C_p(T)$, of its heat capacity, conditioned by processes in the

tetraboride magnetic subsystem. The well defined maximum of this dependence at $T_N \approx 25$ K is conditioned by the tetraboride transition into a magnetically ordered (antiferromagnetic) state [25].

Another phase transformation in SmB_4 around 7 K, conditioned by quadrupolar orbital fluctuations (due to geometrical quadrupolar frustration), is not clearly resolved on the $C_p(T)$ dependence of samarium boride. This transformation corresponds to the inflection point of temperature dependence of the first derivative of the heat capacity (the lower insert in Fig. 1).

The lattice (phonon) contribution, $C_{lat}(T)$, to SmB_4 heat capacity was determined by comparison with the non-magnetic isostructural analogue (LaB_4) [18,29]. The electronic components of the heat capacity, $C_e(T)$, for lanthanum and samarium tetraborides were defined using the low-temperature approximation $C_V(T) = \gamma T + \beta T^3$ (the upper insert on Fig. 1), where the first component on the right-hand side is the contribution of free electrons to tetraboride heat capacity, the second is the sum of magnetic and lattice contributions, and γ and β are the corresponding coefficients (LaB_4 does not have any magnetic contribution). The magnetic component of the heat capacity of SmB_4 is proportional to T^3. This proportionality proves the antiferromagnetic character of the ordered phase of samarium tetraboride. It should be noted that, because of considerably large magnetic contribution to the low-temperature heat capacity of SmB_4, the electronic contribution to the heat capacity of samarium tetraboride is necessarily inaccurate. Therefore, in the first approximation, we assumed that the values of electronic heat capacity for LaB_4 and SmB_4 were similar: $\gamma = 0.74$ mJ·mol^{-1}·K^{-2}.

Fig. 2 shows the lattice heat capacity for LaB_4. The temperature dependence of the SmB_4 lattice heat capacity is the same. The bell-like maximum in the C_V/T^3 vs. T^2 curve, testifies to the presence of the low-frequency Einstein component in the tetraboride lattice heat capacity.

It has been shown [28, 30-33] that a range of different Einstein and Debye contributions can satisfactorily interpolate the experimental temperature dependencies of the substance heat capacity:

$$C_V(T) = \sum_i a_i D\left(\frac{\theta_{D_i}}{T}\right) + \sum_k b_k E\left(\frac{\theta_{E_k}}{T}\right) \quad (1)$$

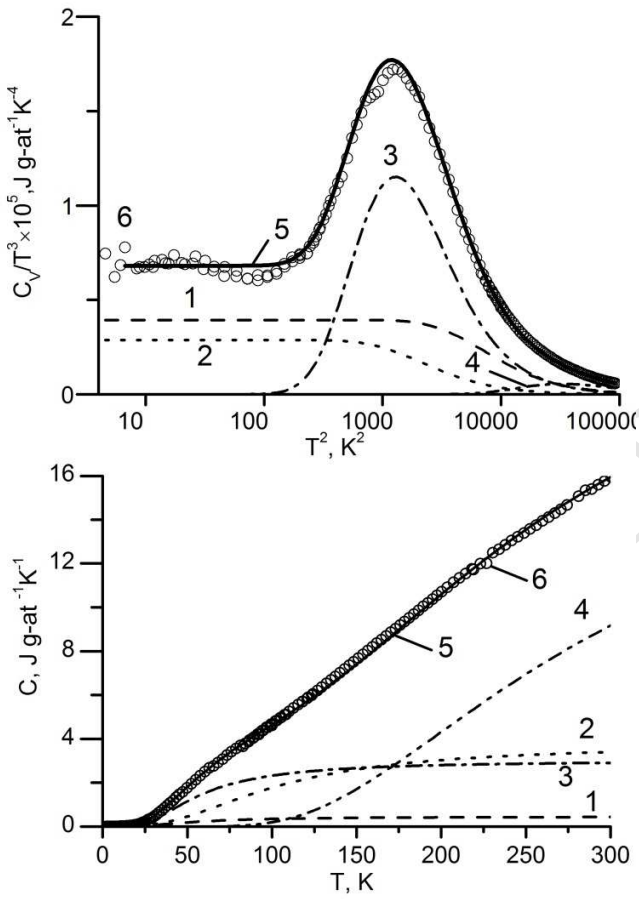

Fig. 2. Lattice heat capacity, $C_{lat}(T)$, of lanthanum tetraboride. 1- $C_{D1}(T)$; 2- $C_{D2}(T)$; 3 - $C_{E1}(T)$; 4 - $C_{E2}(T)$; 5 - ΣC_i; 6 - experimental data.

Here, D and E are the Debye and Einstein functions of heat capacity, respectively; $\theta_{D,i}$ and $\theta_{E,k}$ are the corresponding characteristic temperatures; and a_i and b_k are the weight factors, which define the fraction of the *i*-th (and *k*-th) contribution to the complete heat capacity. To eliminate the arbitrary rule in the choice of correlation parameters of Equation (1), which determine the phonon spectrum form of the tetraborides in this study, we made the following assumptions:

(a) the sum of a_i and b_k values must be close to 1;

(b) the best reproduction of the tetraboride phonon spectrum is possible using such a value set of a_i, b_k, $\theta_{D,i}$, $\theta_{E,k}$, which also satisfactorily describes some other thermal characteristics of tetraboride, for example thermal expansion.

To realise this approach, we experimentally determined the lattice parameters *a* and *c* of SmB_4 and LaB_4 (Fig. 3) between 5 and 300K, according to which the coefficients of linear, $\alpha_a(T)$ and $\alpha_c(T)$, and

volumetric, *β(T)*, thermal expansion were calculated (Fig. 4). The low-temperature characteristic anomalies of the thermal expansion of SmB_4 are evidently conditioned by the processes of magnetic ordering.

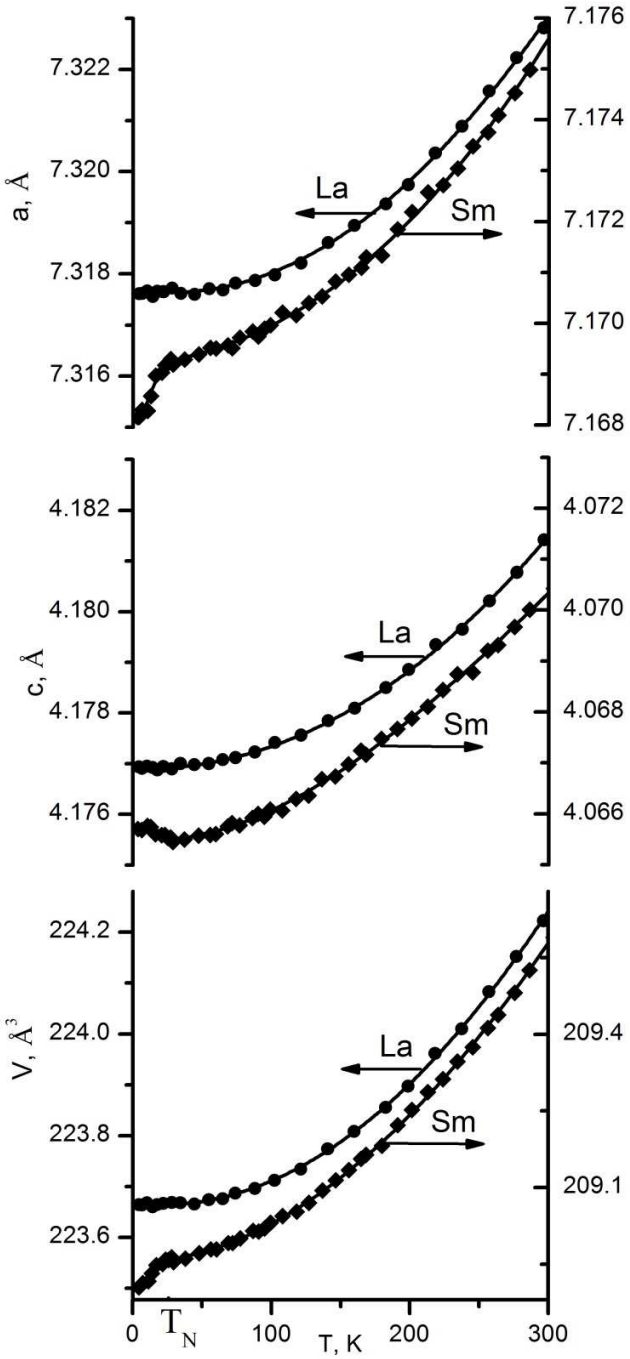

Fig. 3. The lattice parameters *a(T)* and *c(T)*, and the volume of an elementary cell, *V(T)*, for lanthanum and samarium tetraborides.

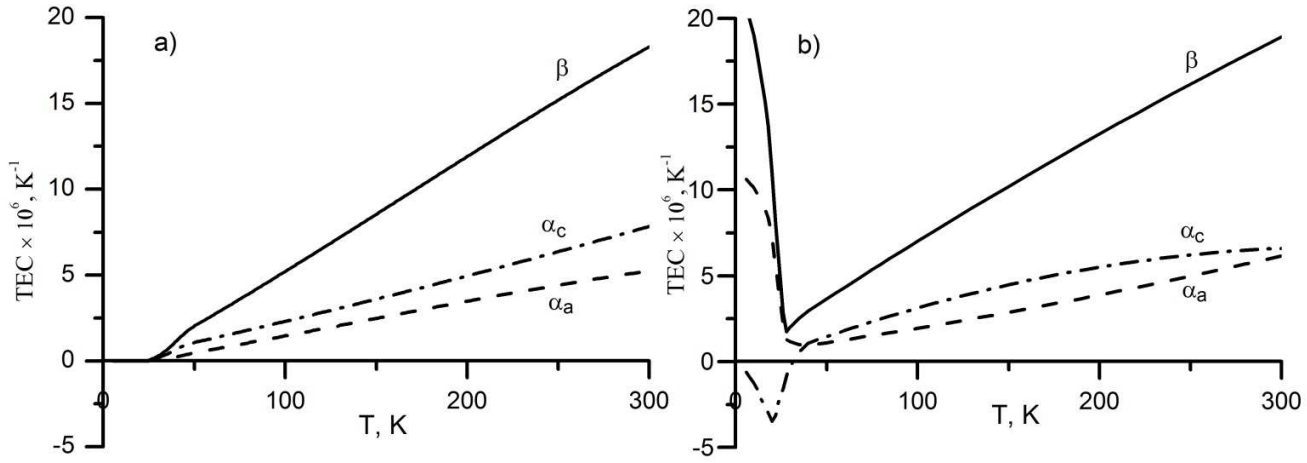

Fig. 4. The coefficients of linear, $\alpha_a(T)$ and $\alpha_c(T)$, and volumetric, $\beta(T)$, thermal expansion of lanthanum (a) and samarium (b) tetraborides.

Table 1. The weight coefficients a_i and b_k, Debye and Einstein characteristic temperatures, $\theta_{D,i}$, and $\theta_{E,k}$, used to approximate the heat capacity and thermal expansion temperature dependencies for lanthanum and samarium tetraborides. In the brackets are given θ_i values, that are determined from Raman spectroscopy data [34].

Sample	a_1	θ_{D1}, K	a_2	θ_{D2}, K	b_1	θ_{E1}, K	b_2	θ_{E2}, K
LaB_4	0.15	420	0.018	230	0.73	890	0.12	177
		(410)		(230)		(893)		(174)
SmB_4	0.175	445	0.015	240	0.72	920	0.11	181
		(444)		(236)		(922)		(180)

According to our estimates, the fit errors δ_k of θ_i values lie within the following range: $\delta_{\Theta D1} \approx \pm 10$K, $\delta_{\Theta D2} \approx \pm 6$K, $\delta_{\Theta E1} \approx \pm 20$K, $\delta_{\Theta E2} \approx \pm 2$K.

Fig. 5 shows the experimental temperature dependence of the relative change, $\Delta V/V_0$, of the volume of a lanthanum tetraboride elementary cell, as well as an approximation using two Einstein and two Debye functions [28,31].

The lattice component of samarium tetraboride thermal expansion was calculated by comparison with data for the expansion of diamagnetic lanthanum tetraboride by the relation [19-21]:

$$\frac{C_{V\,LaB4}(T)}{C_{Vlat\,SmB4}(T)} = \frac{\beta_{V\,LaB4}(T)}{\beta_{Vlat\,SmB4}(T)}$$

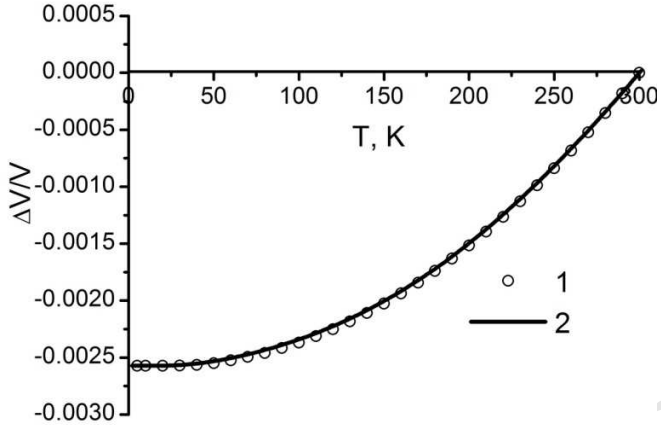

Fig. 5 Relative change of a unit cell volume, $\Delta V/V_0$, for lanthanum tetraboride. 1 – experimental values; 2 - calculated temperature dependence.

Parameters used as approximations for the lattice components of the heat capacity and thermal expansion of LaB_4 and SmB_4 are provided in Table 1. It should be noted that for LaB_4 , for example, the value set of a_1 =0.815, θ_{D1} =1125K, a_2= 0.061, θ_{D2} = 280K, b_1= 0.073, θ_{E1} = 165K, b_2 = 0.06, θ_{E2} = 218K also satisfactorily describes the experimental temperature dependence of heat capacity. As one may see here, $\sum a_i + \sum b_k$= 1.009. When calculating the changes in relative volume for these values of characteristic temperatures (such that the calculated and experimental values of the $\Delta V/V$ parameters should coincide), it is necessary to ascribe the following values: a_1 =0.815, a_2= 0.061, b_1= 0.073, b_2 = 0.06.Thus, $\sum a_i + \sum b_k$=1.159, condition (a) was not satisfied, and the heat capacity approximation using, the aforementioned set of parameters is therefore not satisfactory.

The excess values of the heat capacity $\Delta C(T)$ of SmB_4 is calculated by the subtraction of the electronic and lattice contributions from the total tetraboride heat capacity (Fig. 6). The excess entropy value, $\Delta S(T)$, calculated by the integration of $\Delta C/T$ dependence, was 20.03 J mol^{-1} K^{-1}.

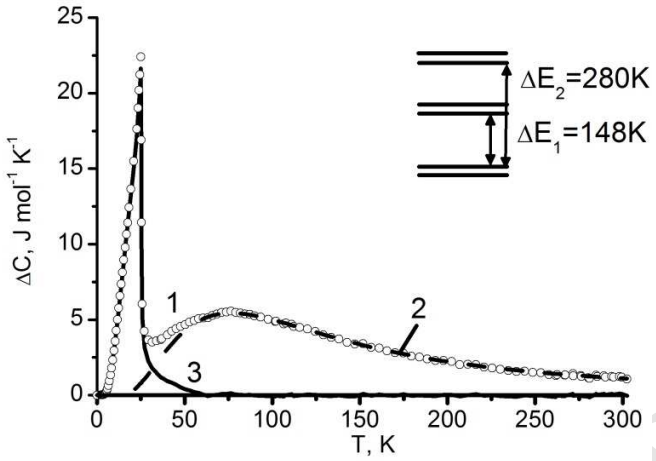

Fig. 6 Components of the excess heat capacity for samarium tetraborides.1 - experimental values; 2 – Schottky contribution $C_{Sch}(T)$; 3 - the magnetic component C_m (T),. The insert illustrates the scheme of splitting of Sm^{3+} ions levels.

This value is considerably higher than the maximum possible change of entropy of ordering the magnetic moments of Sm^{3+} ions: $\Delta S_{m\,max} = R\ln(2J+1) = R\ln 6 = 14.8$ J mol^{-1} K^{-1}. Therefore, we drew the conclusion that one further component (besides the magnetic one) in SmB_4 must contribute towards the excess heat capacity.

The flat maximum of $\Delta C(T)$ dependence in the region of 50 – 80 K was due to the influence of the Crystal Electric Field (CEF) on the electronic subsystem of Sm^{3+} ions.

This influence leads to the emergence of a Schottky contribution in the heat capacity of SmB_4, which is characteristic of many REE compounds.

The CEF energy-level splittings of the f-level Sm^{3+} ions were determined from the measured specific heat using a two-level approximation [18-20, 35,36] in view of the best correlation between the calculated and experimental values. According to our estimates, the fit error of CEF level splitting energies is about ±2 K and ±4 K for ΔE_1 and ΔE_2 accordingly (insert in Fig. 6).

The entropy change of the magnetic subsystem, $\Delta S_m(T)$, at the phase transformation calculated by the integration of $(\Delta C_m/T)/(T)$ dependence is shown in Fig. 7. At $T = T_N$, ΔS_m is close to the value of $R\ln 3$. Clearly, the processes of antiferroquadrupolar ordering at temperatures lower than 7 K can make a considerable contribution, $\Delta S_{m.qu}$, to the total entropy change of the samarium tetraboride magnetic subsystem.

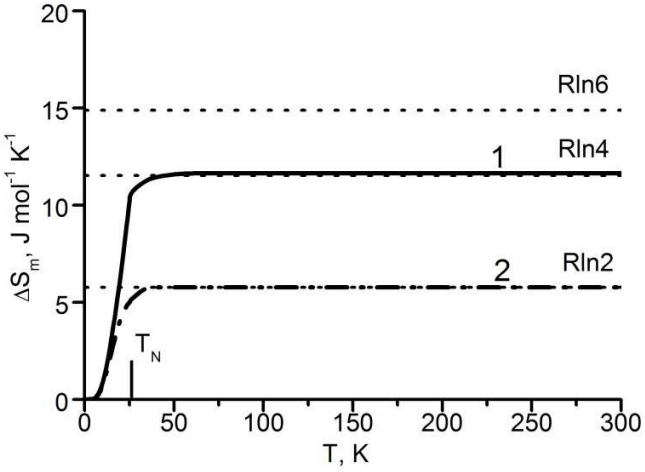

Fig. 7 The entropy of the samarium tetraboride magnetic subsystem. 1 - the temperature dependence of the complete value of entropy, $\Delta S(T)$, which corresponds to the peak of excess heat capacity; 2 – the entropy change of the magnetic subsystem of Sm^{3+} ions in view of the possible contribution of a phase transition at temperatures lower than 7 K .

Taking this contribution into account, the magnetic entropy values (conditioned by the transition of the magnetic moment system of Sm^{3+} ions into an antiferromagnetic state) will be much lower than *R*ln3, approaching *R*ln2 instead. In this case, the ground state of the Sm^{3+} paramagnetic ion is a doublet, which conforms to the aforementioned level splitting scheme by the CEF.

The value of *R*ln4 , which the dependence $\Delta S_m(T)$ approximates with temperature increase, is considerably lower than the maximum possible entropy change in the SmB_4 magnetic subsystem, which is equal to $R\ln(2J+1) = R\ln 6$. This finding testifies to the considerable influence of the frustration of the magnetic moments system of Sm^{3+} ions on the thermodynamic properties of samarium tetraboride. This influence is revealed by the presence of residual (zero-point) entropy on the system of atomic magnetic moments $S_o = R\ln(2J+1) - R\ln 4 = R\ln 1.5$ J mol^{-1} K^{-1}. The even greater value of residual entropy of the samarium tetraboride magnetic subsystem is obtained by taking into account the low-temperature phase transformation mentioned above.

4. Conclusion

Joint calorimetric and X-ray studies of the thermal properties of lanthanum and samarium tetraborides, within a wide range of low temperatures, have made it possible to define an approach for the description of the temperature dependence of their heat capacity and thermal expansion by

combining Debye and Einstein contributions. The values of Debye and Einstein characteristic temperatures conform to the data previously obtained by Raman spectroscopy [34]. It is clear that the proposed approach can be extended to obtain crystalline lattice dynamics parameters for substances belonging to other classes as well. This is made possible using data of their thermal properties alone, without the need to conduct any spectroscopic research.

Comparing our results with data on the properties of lutetium tetraborides has made it possible to demonstrate the influence of lanthanide contraction and of rare earth ion mass, along the row of rare earth tetraborides, on the values of their thermodynamic parameters at both low and high temperatures.

The analysis of the magnetic component of the heat capacity of samarium tetraboride revealed the considerable influence that frustration in the boride magnetic subsystem exerts on the processes of magnetic ordering at temperatures lower than 25 K. It was found that the ground state of Sm^{3+} ions is a doublet. The influence of CEF on SmB_4 thermodynamic characteristics was revealed. To a first approximation, the parameters of ground level splitting were also obtained.

Acknowledgements

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1. The heat capacity and lattice parameters for LaB_4 and SmB_4 were determined at 2-300K.
2. The anomalies of $C_p(T)$, $a(T)$, $c(T)$ for SmB_4 due to the phase transition are revealed.
3. The lattice contributions to the thermal properties of LaB_4 and SmB_4 are analyzed.

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