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ARTICLE

Negative Thermal Expansion and Anomalies of Heat Capacity of LuB₅₀ at Low Temperatures

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Heat capacity and thermal expansion of LuB₅₀ boride were experimentally studied in the 2-300K temperature range. The data reveal an anomalous contribution to the heat capacity at low temperatures. The value of this contribution is proportional to the first degree of temperature. It was identified that this anomaly in heat capacity is caused by the effect of disorder in the LuB₅₀ crystalline structure and it can be described in the soft atomic potentials model (SAP). The parameters of the approximation were determined. The temperature dependence of LuB₅₀ heat capacity in the whole temperature range was approximated by the sum of SAP contribution, Debye and two Einstein components. The parameters of SAP contribution for LuB₅₀ were compared to the corresponding values for LuB₆₆, which was studied earlier. Negative thermal expansion at low temperatures was experimentally observed for LuB₅₀. The analysis of the experimental temperature dependence for the Gruneisen parameter of LuB₅₀ suggested that the low-frequency oscillations, described in SAP mode, are responsible for the negative thermal expansion. Thus, the glasslike character of the behavior of LuB₅₀ thermal characteristics at low temperatures was confirmed.

1. Introduction

The RB₅₀ compounds (R – rare-earth element from Tb to Lu) were intensively investigated as promising thermoelectrics,¹⁻⁵ and attracted attention by their unusual properties. The nature of some of these properties remain unclear so far.

RB₅₀ are the first rare-earth boron-rich compounds, in which magnetic phase transitions at helium temperatures were observed.² The studies proved³ that RB₅₀ compounds are insulators. Despite this RB₅₀ borides demonstrate quite high transition temperatures for such diluted magnetic systems, and therefore strong magnetic interactions. It is characteristic that, for example, HoB₆₆ boride transforms to a spin glass state at the temperature of about 1.1 K⁶, while the magnetic transformation in HoB₅₀ is observed at T=7.5 K².

In the pioneer works^{2,4,5} it was found that RB₅₀ phase is formed with Tb, Dy, Y, Ho, Er, Tm, Yb, Lu. The authors of these works made an assumption that the ordering temperature in RB₅₀ magnetic subsystem is determined by the smallest separation between the boron atoms in B₁₂ icosahedron. They also concluded that B₁₂ icosahedron takes part in magnetic interaction.

As it has been established,⁷ RB₅₀ compounds crystallize in the orthorhombic structure of Pbam space group. The peculiarity of RB₅₀ structure is the ladder position of rare-earth atoms along c axis, parallel to which the chains of B₁₂ icosahedra are

located (Fig.1).

The unit cell for RB₅₀ compounds contains more than 330 atoms. It is characteristic that not all the places in the boron sublattice of RB₅₀ are filled with the boron atoms.² This leads to a certain degree of structural disorder and, as a consequence, to the possible glasslike behavior of a number of their properties at low temperatures.⁸

The analysis of the lattice subsystems in the RB₅₀ borides is appropriate to carry out on the diamagnetic representative of this family – LuB₅₀, whose thermodynamic characteristics at low temperatures are determined only by the properties of its crystal lattice (Lu carries no local magnetic moment and therefore there is no magnetic contribution to the thermodynamic properties).

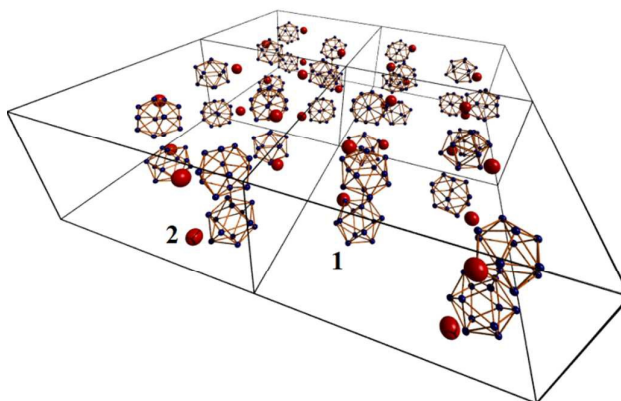


Fig. 1 Crystal structure of RB₅₀. 1 - B₁₂ icosahedra; 2 – rare earth atoms.

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The goal of this study is to experimentally study the temperature dependencies of the thermal properties of LuB_{50} , as well as to determine the influence of the boride structural features on their lattice dynamics.

2. Experiment

The synthesis of LuB_{50} sample was carried out by means of borothermal reduction of lutetium from its oxide in vacuum. For the synthesis we used lutetium oxide of 99.9% purity produced by Mosreaktiv, Russia, and elemental boron of 99% purity produced by ErmakKhim, Russia. The stoichiometric mixture of lutetium oxide and boron powders was pressed in a pellet with the mass of about 5 grams. The synthesis was carried out in a vacuum oven ESKV-1, 2.2, 5/22 ShM3 according to reaction $\text{Lu}_2\text{O}_3 + 103\text{B} \rightarrow 2\text{LuB}_{50} + 3\text{B}_2\text{O}_3$.

At the first stage the pellet was annealed in a vacuum at the temperature of 1700°C for 3 hours. Then the pellet was thoroughly ground, and the resulting powder was sieved several times through the sieve with the cell size of $100\ \mu\text{m}$. At the second short-term heating up to 1000°C the reaction was observed one more time, as the vacuum was temporarily decreased.

The X-ray diffraction pattern of a synthesized sample (Fig.2) corresponded to the ASTM data. The reflexes of the impurity phases were not observed. The lattice parameters of LuB_{50} synthesized sample at the room temperature were equal to: $a = 1.6632\ \text{nm}$, $b = 1.75935\ \text{nm}$, $c = 0.94134\ \text{nm}$. The data on LuB_{50} lattice parameters were not found in the literature. According to the Ref. [2] for ErB_{50} the lattice parameters are $a = 1.6603\ \text{nm}$, $b = 1.7611\ \text{nm}$, $c = 0.9469\ \text{nm}$. Thus, a tendency of decreasing of unit cell volume of RB_{50} borides with the increasing of the rare-earth metal atomic number (lanthanide contraction) was observed.

Heat capacity in the 2-300K temperature range was measured by the automated calorimeter of «THERMAX» Ltd., Russia, by using the adiabatic measuring method with the periodic heating. The measurement error was 3% at 2-15K, then it was decreased to 1% at 60K and remained within these limits at higher temperatures. The calibration measurement on the electrolytic copper sample, that was melted and annealed in a vacuum,⁹ confirmed the said values of the error bars.

The X-ray study of the temperature dependence of the LuB_{50} lattice parameters in the 5-300K temperature range were carried

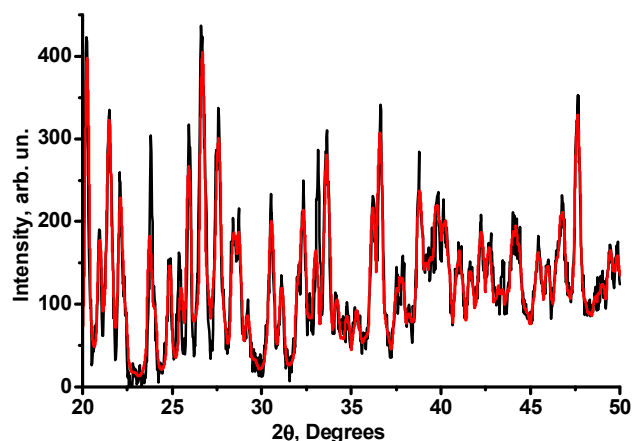


Fig. 2 The X-ray diffraction pattern of LuB_{50} . Red - experimental data; black - calculation by Rietveld-Le Bail method (program "Powder Cell 2.3").

Brentano geometry using $\text{Fe-K}\alpha$ irradiation. The measurements were done using the X-ray diffractometer DRON-7.0 produced by the R&D company Bourestnik (Saint Petersburg, Russia) using the X-ray helium cryostat. The sample temperature during the experiment was measured by the thermocouple «copper + 0.1% iron», which was calibrated using standard germanium (2-20K) and platinum (12-300K) resistance thermometers produced by the All-Russia Research Institute for Physical, Technical and Radiotechnical Measurements (Mendeleev, Moscow Region, Russia). The parameters of LuB_{50} lattice at 5-300K were calculated from the experimental values of the angular position of reflections (502), (452), (514). The experimental errors in determination of the lattice parameters do not exceed $1 \cdot 10^{-4}\ \text{\AA}$. The silicon powder, the small amount of which was added to the sample under study, served as a reference for determining the interplanar distances in LuB_{50} .

3. Results and Discussion

Figure 3 presents the experimental values of the LuB_{50} heat capacity, $C_p(T)$, in the 2-300K temperature range. The curve $C_p(T)$ (Fig. 3a) of the boride does not show any anomalies that could be associated with phase transformations in the sample in the temperature interval under study. However, when plotted as $(C_V/T^3)(T^2)$ (Fig. 3b) the data show a hump at about 40K, as well as a sharp upturn at the lowest temperatures of the experiment.

The first of these anomalies (diffuse peak) can be explained by the heat capacity component corresponding to the Einstein contribution with the characteristic temperature $\Theta_E = 185\text{K}$.^{6,10,11}

The low temperature upturn in the $(C_V/T^3)(T^2)$ curve (Fig. 3b) can be satisfactorily described by the contribution to the heat capacity, which depends on the temperature of a law close to the line: $C_L(T) = 0.00063T^{1.13}$ (Fig.3c). Since there are no phase transformations, temperature-linear contribution to the specific heat can be due to: a) electronic contribution; b) the one-dimensional oscillations of the atomic chains in crystal structure; c) the two-level system excitation, which is characteristic of the disordered (glass-like) states,¹² d) the simultaneous influence of any two or all the three mechanisms listed above.¹³

As LuB_{50} at low temperatures is an insulator, the first of these possibilities can be immediately excluded.

Despite the fact that LuB_{50} is a crystalline compound, as noted above, a large number of atoms in the unit cell, a rather wide homogeneity range of the compound, partial occupancy of boron sites in boric sublattice leads to some a disorder of the crystal structure and, as a consequence, to the glass-like temperature dependence of some properties of boride.

If one assumes the effect of disorder is significantly smaller than the contribution of possible one-dimensional oscillations in LuB_{50} crystal structure, the value $(C_V/T)_{T=0} \approx 0.00063\ \text{J}\cdot\text{g}\cdot\text{at}^{-1}\ \text{K}^{-2}$ (fig. 3c) approximately determines the characteristic temperature Θ_1 of these oscillations: $\Theta_1 \approx \frac{R\pi^4}{0.00063} \approx 130000\ \text{K}$! This absurdly large value of Θ_1 points to the absence of contribution of one-dimensional oscillations to the low-temperature heat capacity of LuB_{50} . Consequently, the close to linear low-temperature component of LuB_{50} heat capacity should be ascribed the influence of the disorder of the crystal structure.

Figure 3b also shows the $(C_V/T)(T^2)$ data for LuB_{66} ¹⁰ for comparison. As seen from the figure, the (C_V/T) vs T^2 dependencies for LuB_{50} and LuB_{66} at low temperatures are considerably different. This difference is due to the different degrees of disorder in the

borides crystal structures, which leads to the significant difference of the potentials in their corresponding two-level systems.

The analysis of temperature dependence of LuB₅₀ heat capacity at low temperatures was performed, as in,¹⁰ in the approximation of soft atomic potentials (SAP) taking into account the Debye contribution: $C_V(T) = C_{SAP}(T) + C_D(T)$.

The nuclear component of heat capacity was considered negligibly small within the temperature range under study and therefore was not taken into account.

According to the model of soft atomic potentials in the disordered systems, apart from usual phonons, there exist the quasi-local low-energy excitations of the three types: two-level systems (TLS),¹⁴ responsible for the glass-like properties at low temperatures,

relaxation systems (RS), in which the transitions are carried out as a result of thermal activation above a barrier, as well as localized and delocalized harmonic oscillators (LHO / DLHO) responsible for the glass-like properties at higher temperatures.^{12,15-18} For different temperature intervals $C_{SAP1} = C_{TLS} = a_1 T$ ($T < 5$ K), $C_{SAP2} = C_{RS} + C_{LHO} = a_2 T^5$ ($5 < T < 10$ K), $C_{SAP3} = C_{DLHO} = a_3 T^2$ ($T > 10$ K).

At the lowest temperatures, the main contribution to the heat capacity in the SAP model is determined by TLS. The component $C_{TLS}(T) = a_1 T$ for lutetium boride was determined by an extrapolation of the linear part of $C_p(T)/T$ vs T^2 dependence to $T = 0$ (Fig. 3c).

At higher temperatures ($10 < T > 5$ K) the main contribution to the heat capacity in the model of soft atomic potentials originates from the relaxation systems (RS), $C_{RS}(T)$, and quasi-local harmonic oscillators (HO), $C_{HO}(T)$. Their contribution for $T > 5$ K is proportional to the fifth power of the temperature: $C_{SAP2}(T) = a_2 T^5$.

As at low temperatures the heat capacity is linear in temperature, $C_{TLS} = a_1 T$, and at higher temperatures it is proportional T^5 , it turns out that in the temperature dependence $C_p(T)/T^3$ there is a minimum, the temperature of which determines the value of the characteristic energy W of two-level systems.

With the further temperature increase, the rapidly increasing density of HO states leads to their delocalization. The heat capacity of the delocalized HO changes proportionally to the square of temperature: $C_{SAP3}(T) = a_3 T^2$. On $C_{SAP}(T)/T^3$ dependence this crossover corresponds to a maximum, the temperature of which, T_{max} , is determined by E_d , energy of the transition from the localized state to the delocalized state of HO: $T_{max} \approx E_d/5k$. The value of delocalization energy E_d , in its turn, determines the frequency of boson peak – the maximum on the frequency dependence of the mode density function to the square of frequency $n(\omega)/\omega^2$: $\omega_d = 2\pi E_d/h$. Further temperature increase leads to the transition of the delocalized soft modes to the Debye limit.¹⁹

The parameters of SAP model for LuB₅₀, that give the best agreement to the experimental data are provided in table 1. The table shows for comparison the literature data for LuB₆₆.¹⁰

As is well known,²⁰ the curve of the lattice heat capacity of a substance, $C_{lat}(T)$, may be approximated by different sets of Debye and Einstein components. Which of these sets correspond to the reality better? In the analysis of experimental temperature dependences of the heat capacity it is necessary to avoid the temptation to introduce too many contributions, that provides a very good correspondence of calculated and experimental values but allows the considerable arbitrariness in the choice of both the number of the Debye and Einstein components, and the corresponding characteristic frequencies of lattice vibrations.

The simplest and the well proven approach is the following.

As a first step we separate the low-temperature glass-like contribution to the specific heat. As a starting set of components only two contributions are considered - one Debye component and one Einstein component.

Their characteristics are easily selected from the analysis of low temperature horizontal section and the maximum in the (C_p/T^3) (T^2) dependence.

It turns out that when you fit satisfactory the low temperature

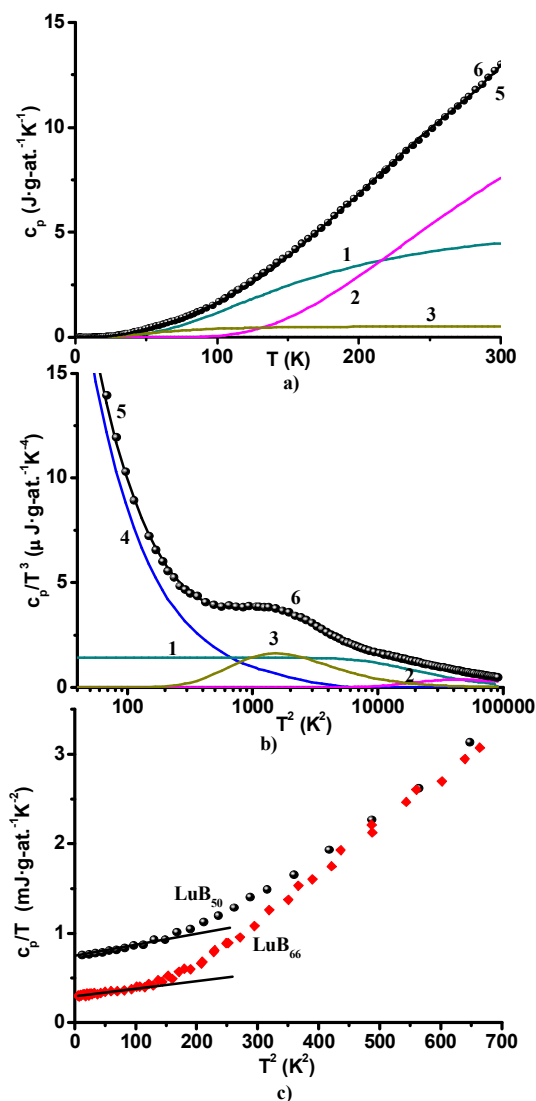


Fig. 3 Heat capacity of LuB₅₀, LuB₆₆. 1- C_D , 2- C_{E1} , 3- C_{E2} , 4- C_{SAP} , 5- $C = \sum C_i$, 6- C_{exp} .

Table 1. Parameters of SAP model for LuB₅₀ (present work) and LuB₆₆.¹⁰

RB _x	T_{max} , K	a_1 , J/mol·K ²	a_2 , J/mol/K ⁶	a_3 , J/mol/K ³	E_d , J	ω_d , c ⁻¹	W , J
LuB ₅₀	42	0.029	$0.99 \cdot 10^{-6}$	$8.7 \cdot 10^{-3}$	$2.90 \cdot 10^{-21}$	$2.741 \cdot 10^{13}$	$7.45 \cdot 10^{-22}$
LuB ₆₆ ¹⁰	24	0.019	$0.40 \cdot 10^{-6}$	$7 \cdot 10^{-3}$	$1.66 \cdot 10^{-21}$	$1.566 \cdot 10^{13}$	$3.31 \cdot 10^{-22}$

dependence of the $C_p(T)$ by two contributions with relatively low characteristic temperatures, at higher temperatures the difference of calculated and experimental data is large. There is a need to introduce into consideration more components. Here it is necessary to take into account the composition and crystal structure of the substance under study. The metal and boron sublattices of LuB_{50} are characterized by a large difference of the masses of atoms (groups of atoms), that form a compound, as well as by the difference in the bond energy of metal and boron sublattices as well as between the boron clusters and between boron atoms forming the boron clusters. These circumstances cause a noticeable difference in the characteristic vibration frequencies of sublattices and between the sublattices. Therefore, it is necessary to consider the introduction of a high-frequency component of Debye and Einstein. Adding each regular component, of course, requires an adjustment of parameters already introduced in consideration of the contributions. The above approach was successfully applied by us in the analysis of the temperature dependence of heat capacity RE-tetraborides.^{21,22}

The resulting analysis of the parameters of the Debye and Einstein contributions satisfactorily comply with spectroscopic data.

The complete experimental temperature dependence of LuB_{50} heat capacity was approximated by SAP contribution $C_{\text{SAP}}=0.00063T^{1.13}$, Debye contribution as well as two Einstein functions (Fig. 3a,b):

$$C_V(T) = C_{\text{SAP}}(T) + k_D C_D\left(\frac{\Theta_D}{T}\right) + k_{E1} C_E\left(\frac{\Theta_{E1}}{T}\right) + k_{E2} C_E\left(\frac{\Theta_{E2}}{T}\right).$$

Here k_j are the weighting factors, characterizing the fraction of the j -th contribution to the boride heat capacity, Θ_j – characteristic temperatures (Table 2).

We have reviewed the contribution to the specific heat, which is proportional $T^{1.13}$. The consideration of the exponent greater than one - is an attempt to take into account the effect of so far ambiguous processes on LuB_{50} heat capacity at low temperatures. Indeed, nearly linear temperature dependence of the specific heat of LuB_{50} dominates at temperatures significantly larger than characteristic temperatures for the glassy state. Possibly a defect mode due to the vacancies in the boron sublattice is present, and, as a consequence, several non-equivalent stable equilibrium positions of RE-ion exist. The transitions between these states may contribute to the heat capacity, which is a similar to Schottky contribution about 10 K.²³

In the absence of the spectroscopic data the assignment of the different modes of approach discussed above to fragments of LuB_{50} structure is rather approximate. However, it is obvious that the optical mode corresponding to the high Einstein characteristic temperature $\Theta_{E1} = 1030\text{K}$, is due to vibrations of the atoms of boron in the boron sublattice of boride (Debye characteristic temperature of elemental boron is 1150K,²⁴ the interatomic distances in the icosahedron B_{12} of RB_{50} and in β -boron are close - about six angstroms).

Significantly smaller value of $\Theta_{E2} = 193\text{K}$, which led to diffuse

maximum on the $(C_p/T^3)(T^2)$ dependence at low temperatures, may be attributed to the local oscillations of much more massive and weakly bound lutetium atoms (see., eg,²⁰). In fact, the Einstein contribution with Θ_{E2} approximates the transition from the localized harmonic oscillators (heat capacity is proportional to T^5) to the delocalized state (heat capacity is proportional to T^2) within SAP model.

The acoustic mode corresponding to $\Theta_D = 680\text{K}$, obviously averages the vibrations of B_{12} clusters, as well as vibrations in the Lu-B bonds.²⁵

Is it possible in any way to confirm the validity of such distribution of modes in structure fragments of LuB_{50} ? Let us consider as a measure of the magnitude of vibration energy the value of $A_i = m_i \Theta_{Ei}^2 \bar{U}_i^2$, where m_i is the mass of the i -th atom, Θ_{Ei} is the characteristic temperature, \bar{U}_i^2 - mean square displacement of the i -th atom from its equilibrium position. Compare the values of A_i for lutetium and boron sublattices in LuB_{50} . Assuming as a first approximation, that the value of \bar{U}_B^2 is approximately half the value of \bar{U}_{Lu}^2 , as it is for RE-hexaborides,²⁶ we obtain $A_B = 10.81 \cdot 1030^2 \cdot \bar{U}_B^2 \approx 11.5 \cdot 10^6 \bar{U}_B^2$, g/mol/K²; $A_{Lu} = 174.97 \cdot 193^2 \cdot 2 \bar{U}_B^2 \approx 13.0 \cdot 10^6 \bar{U}_B^2$, g/mol/K². The similarity of A_B and A_{Lu} values confirms the justification of the mode distribution in the model adopted.

Figure 4 presents the temperature changes of the lattice parameters of LuB_{50} at 5–300K.

The characteristic feature of the dependencies shown in the figure is the region of negative thermal expansion for LuB_{50} at low temperatures. More clearly the negative thermal expansion is seen in the temperature dependencies of the coefficients of linear α_a , α_c and volumetric β thermal expansion (Fig. 5).

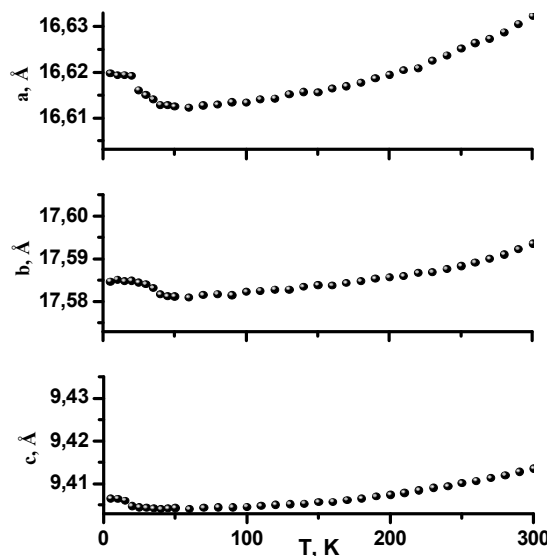


Fig. 4 Lattice parameters of LuB_{50} .

Table 2. The parameters of SAP contribution, the characteristic temperatures of Debye Θ_D and Einstein Θ_{Ej} components of heat capacity, weight factors k_j , Gruneisen mode parameters γ_j for LuB_{50} .

	SAP contribution	j		
		D	E1	E2
Θ_j , K		680	1030	193
k_{SAP}, k_j	0.00063	0.23	0.75	0.022
$\gamma_{\text{SAP}}, \gamma_j$	-3.5	0.8	1	7

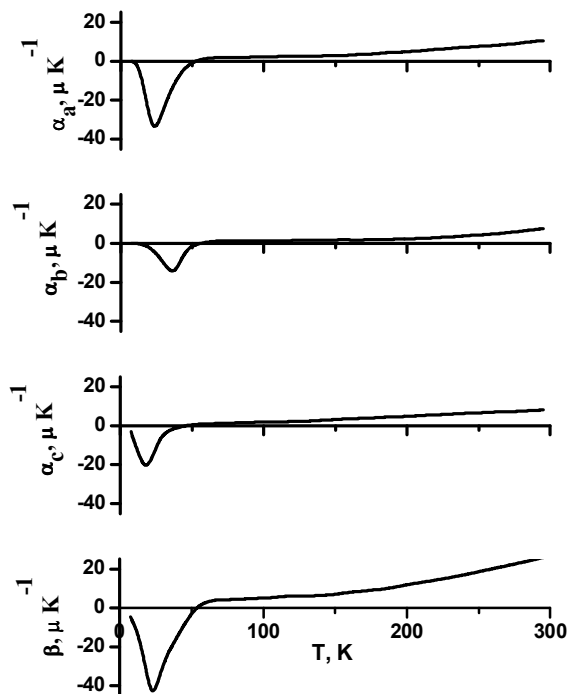


Fig. 5 Linear α_a , α_b , α_c and volumetric β thermal expansion coefficient of LuB₅₀.

To find out the cause of the anomaly stated above, we studied the temperature dependence of the Gruneisen parameter of LuB₅₀ (Fig.6): $\gamma = (\beta V) / (\chi C_v)$. Here V stands for the molar volume, β – volumetric coefficient of thermal expansion (Fig.5), χ – isothermal compressibility, C_v – isochoric molar heat capacity.

We neglected the temperature changes of molar volume in calculating $\gamma(T)$ dependence and assumed its value to be a constant one, equal to $V(T) = V(300K) = 2.07 \cdot 10^{-4} \text{ m}^3/\text{mol}$.

To find the value $C_v(T)$ there was used the approach according to which at $T = \Theta/3$ the remainder $C_p - C_v$ is equal to about 0.01 C_p .^{27,28}

Assuming that the room temperature $T = 300K$ corresponds to $T = \Theta/3$, using the well known relation $C_p - C_v = V\beta^2 T / \chi = 0.01 C_p$, we estimated the value of χ ($\chi = 8.45 \cdot 10^{-12} \text{ Pa}$), and calculated the dependences $C_v(T)$ and $\gamma(T)$.

The experimental dependence of $\gamma(T)$ for LuB₅₀ (Fig.6) was approximated by the equation:

$$\gamma_{\text{calc}} = \frac{\sum_{j=1}^n (\gamma_j C_j)}{\sum_{j=1}^n C_j},$$

where C_j stands for the SAP contribution, Debye and Einstein contributions to the heat capacity calculated according to the values Θ_D , Θ_{E1} , Θ_{E2} , γ_j – mode Gruneisen parameters, characterizing the influence of each mode on the γ value. γ_j values are determined according to the best agreement of $\gamma_{\text{calc}}(T)$ dependence to $\gamma(T)$ experimental dependence (Table 2).

As one can see from figure 6, the calculated dependence of γ_{calc} (T) qualitatively reproduces the features in the $\gamma_{\text{exp}}(T)$ experimental dependence – a relatively small maximum around 50K and a sharp decrease together with the transition to the region of negative values at low temperatures.

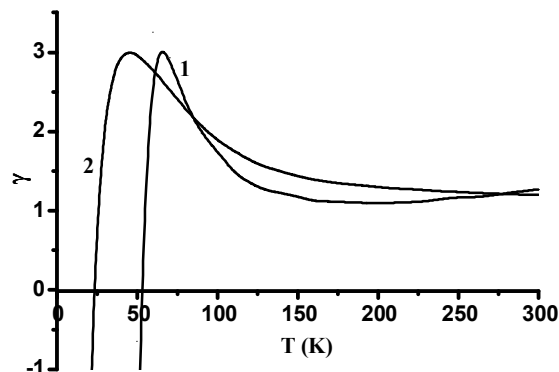


Fig. 6 Gruneisen parameter for LuB₅₀. 1 - exp., 2 - calc..

The inconsistency between the calculated γ_{calc} and experimental γ_{exp} values is due to, on one hand, a considerable inaccuracy in determining of $\beta(T)$, and, consequently $\gamma_{\text{exp}}(T)$, and, on the other hand – by the approximate character of the used model of LuB₅₀ phonon spectrum with one Debye, two Einstein components and SAP contribution.

With all the possible inaccuracy of the γ_j values obtained as a result of fitting, the character of influence of each of them on γ_{calc} value is revealed in the process of fitting quite clearly.

Debye and Einstein contributions with higher characteristic temperatures ($\Theta_D = 680K$, $\Theta_{E1} = 1030K$), as expected, influence the $\gamma_{\text{calc}}(T)$ dependence at the temperature range of 150 – 300K. The maximum of γ_{calc} dependence is mainly affected by the low-frequency Einstein component with $\Theta_{E2} = 193K$.

The abrupt transition of $\gamma(T)$ dependence to the negative region is affected by the influence of the only low-frequency mode which is represented by the oscillations in SAP approximation.

Thus, these oscillations are responsible for the linear character of $C_p(T)$ dependence and the negative thermal expansion LuB₅₀ at low temperatures.

4. Conclusion

The first joint calorimetric and structural, X-ray study of the thermal properties of the RB₅₀ boride family nonmagnetic representative, lutetium boride LuB₅₀ at low temperatures, allowed to determine a number of characteristic properties of the boride phonon subsystem and to carry out their analysis.

The glass-like character of the temperature dependence of LuB₅₀ heat capacity at the lowest temperatures of the experiment is established.

The model of the phonon spectrum for LuB₅₀, consisting of SAP contribution, Debye component and two Einstein components satisfactory reproduces the experimentally obtained features of the temperature dependencies of the heat capacity and thermal expansion.

The close to linear temperature dependence of LuB₅₀ heat capacity at the lowest temperatures of the experiment (2 – 20K) corresponds to the negative thermal expansion of LuB₅₀ in this temperature region and is determined by the low-frequency lattice oscillations in the SAP model.

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