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Heat capacity and thermal expansion of icosahedral lutetium boride LuB_{66}

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Abstract The experimental values of heat capacity and thermal expansion for lutetium boride LuB_{66} in the temperature range of 2–300 K were analysed in the Debye–Einstein approximation. It was found that the vibration of the boron sub-lattice can be considered within the Debye model with high characteristic temperatures; low-frequency vibration of weakly connected metal atoms is described by the Einstein model.

Keywords Heat capacity · Thermal expansion · Low temperatures · Borides

Introduction

The interest in studying the properties of borides, particularly of rare-earth elements with high boron content, is due to the unusual behaviour of the borides' magnetic, lattice subsystems, and the possibility of practical applications [1–5]. The RB_{66} borides series (where R denotes a rare-earth metal) was extensively studied in the latter part of the twentieth century, with investigation of their structural, electric and optical properties and thermal conductivity. In recent works [6–9], the magnetic transformations in some RB_{66} compounds were revealed at temperatures lower than 1 K, a result which was unexpected for substances with such a small concentration of paramagnetic ions.

To successfully study the peculiarities of the magnetic subsystems of substances, it is often necessary to determine effect of the lattice contribution on the overall magnetic characteristics. To achieve this, in the majority of cases, one draws a comparison with the isostructural non-magnetic analogue. For RB_{66} compounds, this analogue is lutetium boride LuB_{66}, which is a diamagnetic substance of the semi-conductive type.

Lutetium boride LuB_{66} has a YB_{66} type cubic crystalline structure, with *Fm3c* space group. For each unit cell, there are 24 formula units (24 metal atoms and 1,584 boron atoms). The large number of crystal voids in the LuB_{66} structure is responsible for a number of its properties, such as its glass-like character. Lutetium atoms fill the voids with centres (0.0589, 1/4, 1/4) and (0.05629, 1/4, 1/4); the occupancy rate is around 0.5.

The boron framework is made up of eight super-icosahedrons $B_{12}(B_{12})_{12}$, each of which consists of thirteen icosahedrons B_{12} (Fig. 1). The peculiarities of LuB_{66} crystalline structure and a large difference in mass between lutetium and boron atoms define the peculiarities of the boride lattice properties.

In the present work, we experimentally studied the temperature dependency of heat capacity $C_p(T)$ and crystalline structure parameter $a(T)$ for lutetium boride LuB_{66} over a broad range of low temperatures, with the purpose of revealing the peculiarities of the behaviour of the phonon sub-system of boride.

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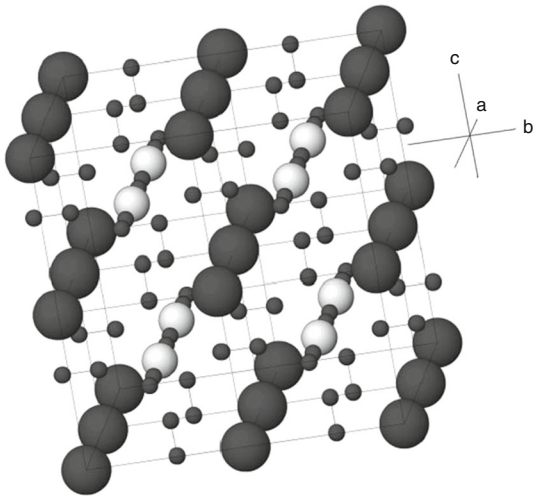

Fig. 1 LuB_{66} structure scheme [2]. *Larger dark circles* super-icosahedrons$(B_{12})_{13}$, *smaller light circles* B_{80} clusters, *dumb-bells* Lu atoms

Experiment

A powdered lutetium boride LuB_{66} sample was obtained via boron-thermal metal reduction from the oxide in a vacuum:

$$Lu_2O_3 + 143B = 2LuB_{70} + 3BO \uparrow .$$

After the homogenising anneal at 1,000 °C, and melting in the arc furnace, the amount of boron in the lutetium boride decreased as its composition got closer to that of the stoichiometric case. The X-ray diffraction pattern of synthesised lutetium boride contained peaks associated with the only LuB_{66} phase as compared with the ASTM data file. According to the chemical analysis, the sample composition was 19.6 % Lu, 80.2 % B and 0.09 % O_2. The pycnometric mass density of the sample, ρ_{pycn}, was 2.430×10^3 kg m^{-3}, which is 93 % of the X-ray density value. The difference between the X-ray and pycnometric density is caused by the porosity of the sample. Spectral analysis showed the presence of a small amount of tungsten admixture in the sample, amounting to around 1 % of the lutetium content.

The heat capacity of the LuB_{66} samples, at temperatures from 2 to 300 K, was measured in a calorimeter (Termax Ltd.). The calorimeter implements the classical adiabatic method of heat capacity investigation [10, 11]. The experimental error at 1.8–4.2 K is about 3 %, at 4.2–40 K is 2 % and at 40–350 K is 0.5 %.

The lattice parameter $a(T)$ of LuB_{66} in the range of 5–300 K was determined using a X-ray diffractometer (DRON-7.0) in the Co-Kα radiation mode, with use of a helium cryostat. The calculation of $a(T)$ values was made based on the experimental angular positions of 12 Bragg reflections [12]. The error in calculating the $a(T)$ lattice parameter of LuB_{66} was $\pm 10^{-4}$ nm.

At room temperature, the value of $a(T)$ was 23.3850 Å, which agrees well with values quoted in the literature ($a = 23.412$ Å, [13]).

Results and discussion

The experimental temperature dependence of heat capacity $C_p(T)$ for lutetium boride LuB_{66} (Fig. 2) does not contain any visible anomalies; however, if the date are plotted as C_p/T versus T^2 (inset in Fig. 2) and C_p/T^3 versus T^2 coordinates (Fig. 3), one can see that at low temperatures ($T < 10$ K), the values of the boride heat capacity are anomalously high, and at $T = 30$ K there is an anomaly similar to the Einstein component of heat capacity.

The values of the crystalline structure parameter $a(T)$ obtained in the present work are shown in Fig. 4, alongside the calculated temperature dependence of the coefficient of thermal linear expansion $\alpha(T)$ for lutetium boride LuB_{66}, in the interval of 5–300 K. $a(T)$ and $\alpha(T)$ dependencies, similar to the $C_p(T)$ dependency, does not exhibit any visible anomalies in the temperature range studied.

The analysis of the temperature dependence of heat capacity and the thermal expansion of LuB_{66} boride was made on the basis of the combined approach of Debye–Einstein.

For heat capacity:

$$C_v = k_1 D\left(\frac{T}{\Theta_{D_1}}\right) + k_2 D\left(\frac{T}{\Theta_{D_2}}\right) + k_3 E\left(\frac{T}{\Theta_E}\right) + k_4 T, \quad (2)$$

where D is the Debye function; E is the Einstein function; k_i is the fraction of the i-th contribution to the boride total heat capacity; and Θ_{D_i} and Θ_E are characteristic temperatures [14]. The latter term describes the glass-like contribution, which linearly depends on the temperature [15–17].

For thermal expansion:

$$\Delta V(T)/V(T_0) = [V(T) - V(T_0)]/V(T_0) = (x_T - x_{T_0})/x_{T_0}$$
$$x_T = \frac{3g}{4c^2}(\varepsilon - G\varepsilon^2 - F\varepsilon^3), \quad (3)$$

where:

$$\varepsilon = k_1 D\left(\frac{T}{\Theta_{D_1}}\right) + k_2 D\left(\frac{T}{\Theta_{D_2}}\right) + k_3 E\left(\frac{T}{\Theta_E}\right).$$

Here, Θ_{D_i} and Θ_E are the characteristic Debye and Einstein temperatures, respectively; the parameters G, F, c, g, f characterise the anharmonic component of the interatomic interaction potential in the crystal; and $T_0 = 300$ K [18].

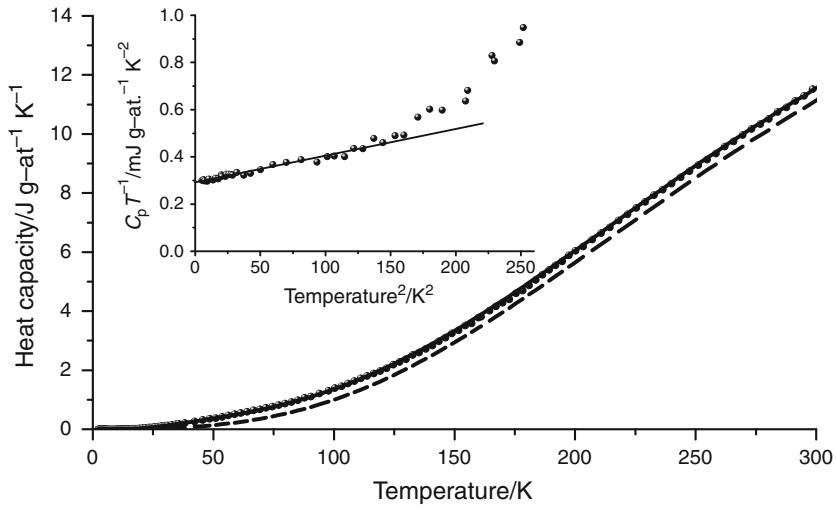

Fig. 2 Temperature dependence of lutetium boride LuB_{66} heat capacity. *Points* experimental data. *Solid line* calculated values [the relation (2)]; *dashed line*—the same, but without the Einstein contribution. *Inset* illustrates the presence of the contribution to the heat capacity at the lowest temperatures, which is proportional to 1st power of the temperature

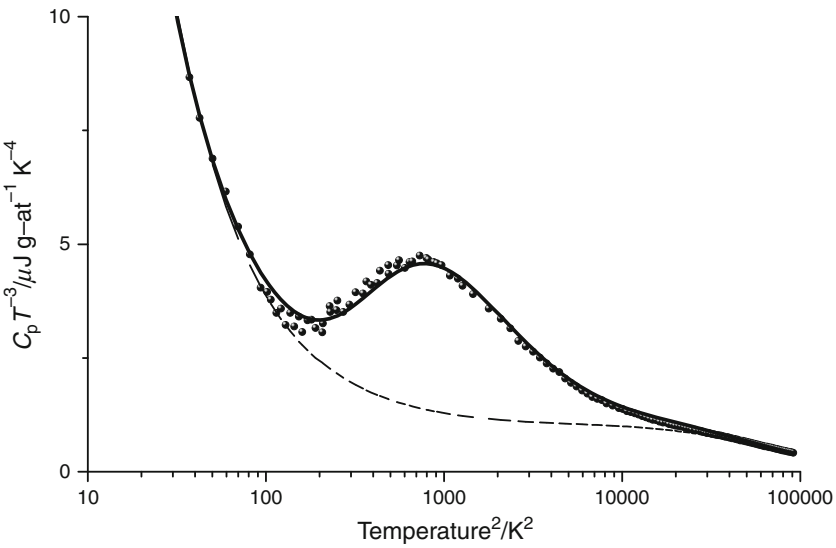

Fig. 3 Dependence of C_P/T^3 from T^2. *Points*, the *solid line*, *dashed line*—the same as in Fig. 2

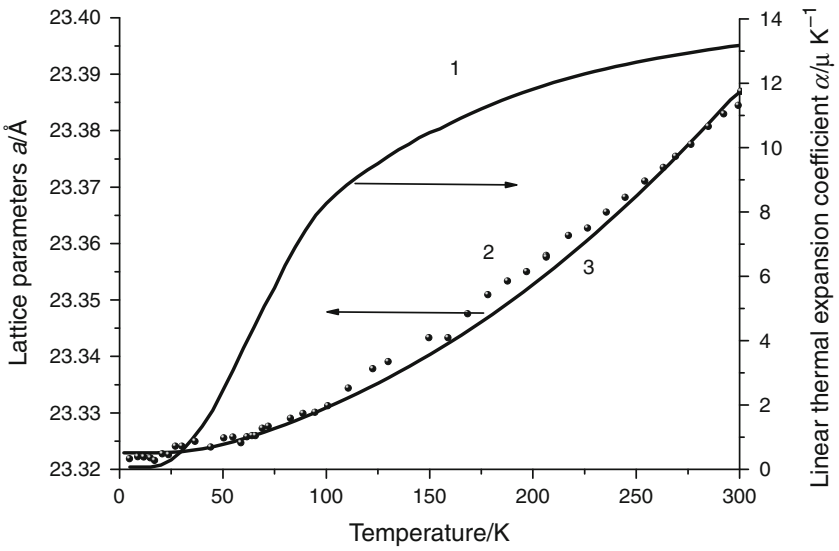

Fig. 4 Lattice parameter $a(T)$ (*1*) and linear thermal expansion coefficient (*2*) for lutetium boride LuB_{66}, and approximate computation (*3*)

Table 1 The characteristics of LuB_{66} lattice dynamics according to calorimetric and X-ray data

$C_v(T)$, Jg at/K							$\Delta a/a(T)$					
Θ_{D_1}	k_1	Θ_{D_2}	k_2	Θ_E	k_3	k_4	Θ_{D_1}	k_1	Θ_{D_2}	k_2	Θ_E	k_3
1,360	0.9	800	0.08	140	0.017	0.00029	1,360	0.91	790	0.08	142	0.3

In Table 1, the approximate parameters for Eqs. (2) and (3) are provided, which were obtained by the least squares fit to the experimental data.

As can be seen in Figs. 2 and 3, we managed to describe the experimental dependencies of $C_p(T)$ and $\Delta V/V(T)$ for lutetium boride in the $T < 300$ K temperature range, following the process of approximating different thermal characteristics and using accepted approximations for similar values of characteristic temperature.

The high values of characteristic temperatures Θ_{D_1} and Θ_{D_2} can be ascribed to the boron sub-lattice, where the first value, Θ_{D_1}, characterises the vibration of boron atoms in the sub-lattice, and the second value may characterise the vibration of boron clusters B_{12}, which are the basic structural components of the boron sub-lattice. We should note that the characteristic temperatures of elemental boron, according to different publications, are 1,540, 1,300 and 1,200 K [19]. The vibration of lutetium atoms in a boride can be described by the Einstein model with comparatively low characteristic temperature $\Theta_E = 140$ K, which closely matches $\Theta_D = 184$ K (equivalent to $\Theta_E = 138.4$ K) [20] for metallic lutetium, and is close to Θ_E, which is calculated according to the frequency of delocalisation of HO in the soft atomic potentials (SAP model): $\Theta_E = \hbar\omega/k = 119$ K [21].

The obtained distribution of characteristic temperatures in the LuB_{66} boride sub-lattice is consistent with the fact that for the calorimetric data, the ratio $(k_1 + k_2)/k_3$ amounts to =62, which is close to the ratio of boron atoms to lutetium atoms in a LuB_{66} molecule.

One cannot help noticing the considerable difference between the coefficients of the Einstein component k_3 in the approximation of the calorimetric data and the thermal expansion values. In this case, if heat capacity $\sum_{i=1}^{3} k_i = 0.997$, *i.e.* close to 1 (one), as it has to be, then for thermal expansion a much greater value k_3 leads to $\sum_{i=1}^{3} k_i = 1.29$. We should note that while conducting similar analysis of the thermal properties of rare-earth tetraborides [22] (unpublished work), we revealed the twofold excess of k_3 values obtained from X-ray data, over the calorimetric values of this coefficient. The sum $\sum_{i=1}^{3} k_i$ for X-ray data also turned out to be more than one, although in this case it was marginal. Such anomalous behaviour of X-ray k_3 values is not clear and needs further study.

From the outlined arguments, looms the following picture: low-temperature data on heat capacity and thermal expansion for rare-earth borides can be described with the help of the Debye–Einstein combined approach; the values of the Debye components, describing the vibration of the boron sub-lattice, turn out to be similar for calorimetric and X-ray data; low-frequency vibrations, which we ascribe to the metal sub-lattice within the Einstein approximation, largely affect borides heat capacity at low temperatures and thermal expansion in the middle part of low-temperature region.

Conclusions

Calorimetric and X-ray research into the thermal properties of icosahedral lutetium boride LuB_{66} in the broad interval of low temperatures and the analysis of experimental data in the Debye–Einstein approximation enabled us to determine the character of ion oscillations in boron and metallic sub-lattices of a boride and to define the sub-lattices characteristic temperatures. It was found that vibrations in the boron sub-lattice, which are characterised by comparatively small masses of atoms and high values of bond energy, can be satisfactorily described by the Debye model. The vibrations of massive and comparatively weakly bonded lutetium atoms can be described well by the Einstein approximation. The latter conclusion clarifies why in earlier works [12, 22–24], it was difficult to separate the electronic and lattice contributions to the low-temperature heat capacity of rare-earth tetraborides in the simplest approximation, $C_v = aT + bT^3$: the lattice contribution, besides the cubic Debye term, contains the Einstein component.

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