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Defect Mode in LaB_6

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The specific heat of high quality La^NB_6 ($N = 10$, 11, natural) single crystals is investigated in a wide range of temperatures 2 – 300 K. The obtained data allow to estimate correctly (i) the electronic $\gamma \cdot T$ term of specific heat ($\gamma \approx 2.4$ mJ/(mol·K^2)), (ii) the contribution from quasilocal vibrating mode of La^{3+} ions ($\Theta_E \approx 150$ – 152 K), (iii) the Debye-type term from rigid boron cages ($\Theta_D \approx 1160 \pm 40$ K). Our data also suggest an additional defect-mode component (iv) which may be attributed to a contribution of 1.5% boron vacancies in LaB_6. The obtained results may be interpreted in terms of formation of two level systems, which appear when La^{3+} ions are displaced from their centrosymmetric positions in the cavities of rigid boron cages, apart from randomly distributed boron vacancies in the LaB_6 matrix.

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1. Introduction

Lanthanum hexaboride (LaB_6) has been the subject of many studies over the years (see the review in [1]). Unlike the other RB_6 compounds, which properties are influenced by the complicated interplay of various degrees of freedom, nonmagnetic LaB_6 is the ideal object of thermodynamical investigations. As all hexaborides, LaB_6 has a simple bcc structure of CsCl type (s.g. $Pm3m{-}O_h^1$) with rare earth (RE) ions in the body centered positions and boron octahedra in the cube corners. The unique property of such structure is that it may be divided into two classes. The boron atoms are coupled by strong covalent bounds forming the Debye sublattice. On the other hand, due to their loosely bound state, the La^{3+} ions are treated as independent harmonic oscillators (Einstein oscillators). Therefore, LaB_6 is a model object for specific heat studies. Although the procedure of specific heat analysis was published for LaB_6 in many works [2 – 5] the most of them do not discuss the contribution of the defect mode predicted previously for RB_6 by Kasuya [6]. Thus, it is of interest to compare our conclusions with results of [2 – 5].

2. Experimental details

The specific heat of LaB_6 single crystals was studied at constant pressure over a wide temperature range 2 – 300 K in PPMS-9 (Quantum Design). In order to detect the defect-mode contribution La^NB_6 single crystals with various boron isotope content ($N = 10$, 11, nat.) were additionally studied. The quality control of the samples was performed by electron microprobe and X-ray diffraction (XRD) analysis.

3. Results and discussion

The temperature dependences of specific heat $C(T)$ of La^NB_6 are presented in Fig. 1. The obtained data agrees rather well with that of [4, 5] beyond the temperature interval of 4.2 – 20 K, where the defect-mode dominates. Other contributions to specific heat were calculated in the framework of standard procedure previously applied in [2, 5]. To estimate the electronic term $C_{el} = \gamma \cdot T$ we took the value $\gamma \approx 2.4$ mJ/(mol·K^2) which is close to the results of electronic structure calculations [7] and previous specific heat analysis of LaB_6 [2, 5]. The phonon

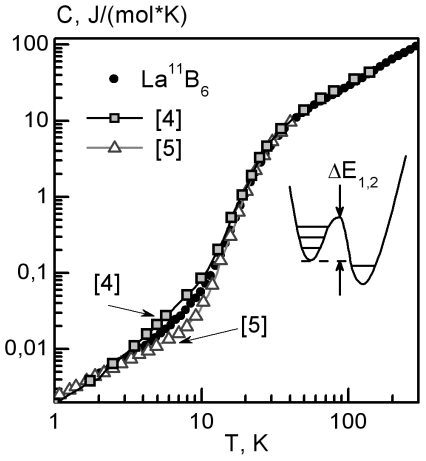

Fig. 1. Temperature dependences of specific heat of $La^{11}B_6$ with data taken from [4] (symbols □) and [5] (symbols △).

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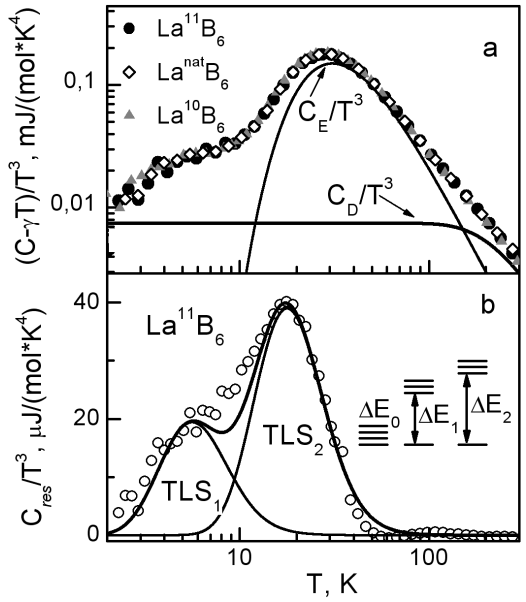

Fig. 2. (a) Separation of the phonon contribution $(C-\gamma\cdot T)/T^3$ into Debye C_D/T^3 and Einstein C_E/T^3 components. (b) The analysis of residual contribution C_{res}/T^3 by Schottky relation with two types of TLS (see the text).

contribution $C_{ph}/T^3 = (C-\gamma\cdot T)/T^3$ is studied in Fig. 2a. The Einstein term C_E of the R^{3+} quasi-local vibrational mode and Debye term C_D of the rigid boron cage were separated with temperatures $\Theta_E \approx 150 - 152.5$ K and $\Theta_D \approx 1160$ K, which agree well with the results of specific heat studies [2–5] and lattice dynamics investigation (see the review [1]).

Let us consider the defect mode contribution to the specific heat of LaB_6. Following the subtraction of the sum C_D/T^3 and C_E/T^3 from C_{ph}/T^3 one can calculate the residual contribution C_{res}/T^3 presented in Fig. 2b. In our opinion, C_{res}/T^3 describes the defect mode term induced by the presence of boron vacancies in the RB_6 matrix. Indeed as it was predicted in [6] and then proved by the results of point contact spectroscopy [8], XRD and neutron diffraction investigations (see for example [9]), there are about 1-9% of vacancies in the boron sublattice in RB_6. The presence of boron vacancies in combination with loosely bonded states of RE ions leads to a displacement of some of R^{3+} ions from their central positions inside the B_{24} cells in RB_6. Therefore in addition to the main centrosymmetric site there are also several nonequivalent off-centered positions of R^{3+} ions. In such situation the effects of disorder in RE ion's position are responsible for two-level systems (TLS) formation, or equivalently, the appearance of double-well potential (DWP) typical for glasses [10] (see also the inset in Fig. 1). The existence of DWP with barrier height of ΔE_i leads to tunnelling of electrons between the TLS states. Thus to calculate the TLS characteristics we described the residual contribution C_{res}/T^3 by the Schottky relation

$$C_{TLSi} = \frac{g_1 N_i}{g_0}\left(\frac{\Delta E_i}{T}\right)^2 \frac{\exp\left(-\Delta E_i/T\right)}{\left(1+g_1/g_0\exp\left(-\Delta E_i/T\right)\right)^2}, \qquad (1)$$

with two types of TLS consisting of singlet (g_0) and triplet (g_1) states (see Fig. 2b). It was found that both the concentration of TLS_2 $N_2 \approx 0.06$ and the barrier height $\Delta E_2 \approx 92$ K do not depend on the boron isotope content. Therefore, we propose that TLS_2 is related to boron vacancies contribution. Taking into account the details of RB_6's local structure, where one boron vacancy belongs to four neighboring cells, the real vacancy concentration is determined by the relation $n_{vac} = N_2/4 = 1.5\%$. Note that the defect mode contribution of LaB_6 may also be estimated from data presented in [4, 5]. Moreover, the existence of TLS was experimentally detected from the recent Raman spectra investigations of LuB_{12} [11], which is a nonmagnetic analog of LaB_6. The detailed analysis of specific heat of LaB_6 will be presented elsewhere.

4. Conclusions

The analysis of specific heat of LaB_6 is presented. The obtained data allows to deduce a defect-mode contribution which originates from 1.5% of boron vacancies in LaB_6.

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