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Heat capacities of the $YAl_3(BO_3)_4$, $GdAl_3(BO_3)_4$ and $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$ borate crystals

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Results of heat capacity measurements for the $YAl_3(BO_3)_4$ and $GdAl_3(BO_3)_4$ single crystals and for their solid solution $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$ are presented. The measurements were carried out in a wide temperature range from 1.9 to 300 K. Temperature dependencies of heat capacity were treated within the framework of the Debye and Einstein models and Schottky anomalies. Abnormal additional contribution to the solid solution heat capacity near 7 K was treated assuming the existence of excessive low-frequency oscillatory states associated with the substitutional disorder of yttrium and gadolinium ions over the crystalline lattice sites.

Keywords: heat capacity, alumoborates, Debye and Einstein contributions, Schottky anomaly, substitutional disorder.

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1. Introduction

Borate crystals with the general formula $ReM_3(BO_3)_4$, where Re is a trivalent ion of a rare earth element or yttrium, and M is trivalent ions of Al, Ga, Fe, Sc or Cr, as well as their solid solutions, are known as phosphors, promising for use as materials for LEDs, scintillators and displays, in luminescent thermometry and laser technology, as well as nonlinear media for frequency doubling (see [1] and references in this paper). However, despite the prevalence of such crystals, their thermal properties are poorly understood. The heat capacity of yttrium aluminum borate $YAl_3(BO_3)_4$, widely used as a crystal matrix for doping with paramagnetic rare earth ions, was studied in [2–4]. The heat capacity of yttrium and gadolinium aluminum borates was measured in Ref. [2] in the temperature range from 6 to 300 K. The results were interpreted within the Debye model with a temperature-dependent characteristic temperature. The heat capacity of crystals $YAl_3(BO_3)_4$ and $EuAl_3(BO_3)_4$, weakly doped with cobalt ions, was measured in Ref. [3] in the range from 3 to 395 K. The analysis of experimental data was carried out on the basis of the Debye model, taking into account the contribution of dispersionless modes within the framework of the Einstein model. The results of a study of the heat capacity of yttrium aluminum borate in the high-temperature range from 329 to 1051 K are provided in Ref. [4].

This paper presents the results of a study of the heat capacity of $YAl_3(BO_3)_4$, $GdAl_3(BO_3)_4$ crystals and a solid solution $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$ in the range from 1.9 K to room temperature in order to analyze phonon contributions to the heat capacity and Schottky anomalies caused by the presence of magnetic gadolinium ions.

2. Samples and experiment

Single crystals $YAl_3(BO_3)_4$, $GdAl_3(BO_3)_4$ and $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$ were obtained by the melt solution growth method. The studied oxides crystallize into the hantite structure $CaMg_3(BO_3)_4$, space group $R32$ [5]. The samples for measuring the heat capacity were cut from single crystals in the form of plates with a surface of about 3×3 mm and a thickness of about 0.5 mm. The mass of the samples was 18.06, 17.46 and 17.65 mg for $YAl_3(BO_3)_4$, $GdAl_3(BO_3)_4$ and $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$, respectively.

The heat capacity was measured on the Quantum Design PPMS-9+EverCool-II unit using the built-in option in the temperature range 1.9–300 K in a zero magnetic field.

3. Results and discussion

Figure 1 shows the dependences of the heat capacity C in the studied crystals on the temperature T. In the curves for samples containing gadolinium ions, an increase in heat capacity with a decrease in temperature is observed at low temperature, which is absent in the curve of heat capacity for yttrium aluminum borate.

Figure 2, $a-c$ shows the dependences of the heat capacity divided by the temperature in the third degree calculated from the experimental data shown in Figure 1. These dependences show wide maxima near 30 K, shifting to low

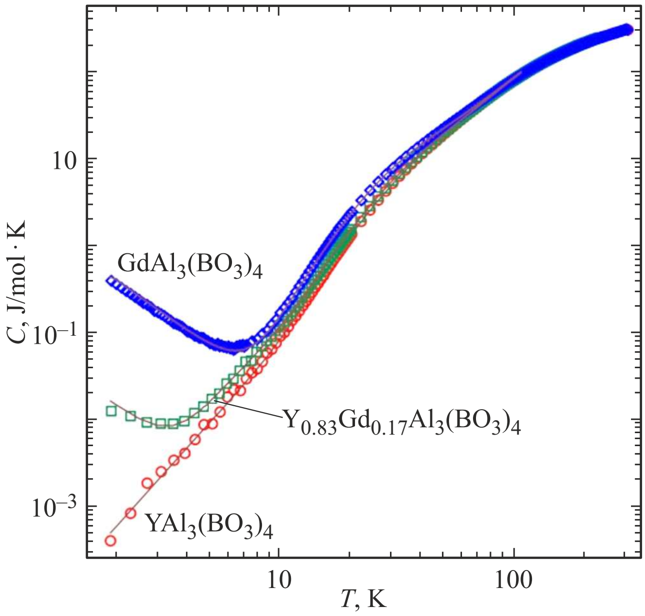

Figure 1. Experimental dependences of heat capacity on temperature (symbols) and fitting curves in the range from 1.9 to 100 K (solid lines) for the studied borates.

temperatures with increasing gadolinium content. Maxima of this type on curves C/T^3 have been observed in various materials, both in single crystals and in ceramics (see, for example, [6–8]). Their appearance is attributed to the deviation of the phonon contribution to the heat capacity from the Debye model due to the presence of optical modes with weak dispersion. The Einstein model [9] is used to interpret the contribution of dispersionless vibrational modes.

Additional features of the heat capacity in gadolinium-containing crystals at temperatures below 10 K are related to the population of the Stark energy levels of magnetic ions in the crystal field. The increase in heat capacity compared to the phonon contribution is considered as a contribution of Schottky anomalies [9].

Thus, in the theoretical interpretation of the temperature dependences of the heat capacity in the studied aluminum borates, lattice vibrations should be taken into account as the sum of the Debye and Einstein contributions and the contribution of Schottky anomalies. Debye's molar heat capacity is written as [9]

$$C_D(T) = 3r_D R\left(\frac{T}{\theta}\right)^3 \int\limits_0^{\theta/T} \frac{x^4 e^x}{(e^x-1)^2}\,dx, \qquad (1)$$

where r_D is the number of vibrational modes interpreted within the Debye model, R is the gas constant, θ is the Debye temperature. The molar heat capacity in the Einstein model is

$$C_E(T) = r_E R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}, \qquad (2)$$

where θ_E is the Einstein temperature and r_E is the number of vibrational modes taken into account in the Einstein model. It should be noted that the sum of the parameters r_D and r_E should be equal to 60 — tripled the number of atoms in the formula unit.

The contribution to the heat capacity of Schottky anomalies is represented as [9]

$$C_S = \frac{nR}{T^2}\left[\frac{\Sigma_i \Delta_i^2 g_i e^{-\Delta_i/T}}{g_0 + \Sigma_i g_i e^{-\Delta_i/T}} - \left(\frac{\Sigma_i \Delta_i g_i e^{-\Delta_i/T}}{g_0 + \Sigma_i g_i e^{-\Delta_i/T}}\right)^2\right], \qquad (3)$$

where n is the number of magnetic ions of a certain type in the molecular formula, Δ_i — is the energy difference in kelvins between the ground level, which corresponds to the index $i = 0$, and the excited level with the number $i \geq 1$, g_0 and g_i is the degeneracies of the ground and excited states.

To analyze the heat capacity in yttrium aluminum borate, which does not contain magnetic ions, only the phonon contribution should be taken into account according to the formulas (1) and (2).

Let us first consider the theoretical interpretation of the heat capacity in yttrium and gadolinium aluminum borates. Infrared absorption spectra in aluminum borates of various compositions were studied in a wide frequency range in Ref. [10]. For crystals with $R32$ symmetry, including yttrium and gadolinium aluminum borates, two lines in the low-frequency region were observed, attributed to translational vibrations of rare earth ions or yttrium. The wave vectors of these vibrations have values of about 100 cm^{-1} (144 K) and decrease with increasing ion mass Re^{3+}. Thus, the appearance of maxima on the C/T^3 temperature dependences for crystals of $YAl_3(BO_3)_4$ and $GdAl_3(BO_3)_4$ should be associated with Einstein's contributions from two optical modes that correspond to the vibrations of yttrium and gadolinium ions, respectively. The shift of the maximum to low temperatures for gadolinium aluminum borate compared with the maximum for yttrium borate correlates with the shift of line frequencies in the infrared spectra. The result of approximating the heat capacity of a $YAl_3(BO_3)_4$ crystal divided by the cube of temperature, based on the Debye model, taking into account two Einstein contributions, is shown in Figure 2, *c*. Debye temperature θ, two Einstein temperatures θ_{E1} and θ_{E2}, coefficients r_D, r_{E1} and r_{E2} played the role of fitting parameters. A good agreement with the experiment was obtained when the Debye temperature was 800 K for all three samples. The remaining obtained approximation parameters are shown in the table. It should be noted that the calculated values of the Einstein temperatures are close to the frequencies of translational vibrations of yttrium ions found in Ref. [10]. Figure 2, *c* also show the individual Debye and Einstein contributions. The theoretical dependence of the heat capacity within the framework of the approach used is shown in Figure 1. There is excellent agreement with experimental results below 100 K, which demonstrates the applicability of the Debye model, taking into account only

Fitting parameters

Sample	θ_{E1}, K	θ_{E2}, K	r_D	r_{E1}	r_{E2}	Δ, K	θ_{exc}, K	r_{exc}
$YAl_3(BO_3)_4$	108	187	57.3	0.5	2.2	–	–	–
$Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$	see text		57.29	see text		0.18	30	0.006
$GdAl_3(BO_3)_4$	80	143	57.25	0.35	2.4	0.4	–	–

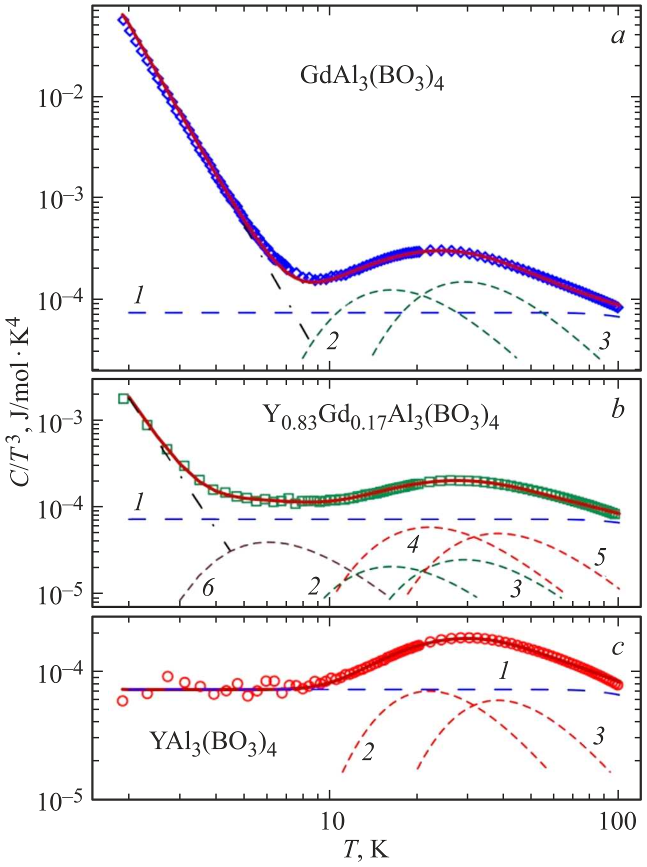

Figure 2. Temperature dependences of experimental values of heat capacity divided by temperature to the third power, (symbols) and theoretical curves (solid lines) for (*a*) aluminum gadolinium borate, (*b*) a solid solution of yttrium and gadolinium aluminum borates, (*c*) yttrium aluminum borate. Dashed lines show individual contributions. Digit *1* indicates Debye's contribution. The numbers *2* and *3* on the graphs (*a*) and (*c*) indicate Einstein's contributions due to low-frequency optical vibrations. On the graph (*b*) *2* and *3* — Einstein's contributions from Gd^{3+} ion vibrations, *4* and *5* — Einstein's contributions from Y^{3+} ion vibrations, *6* — additional contribution from excessive low-frequency vibrations.

two Einstein contributions over the entire temperature range from 1.9 to 100 K.

It is necessary to consider the additional contribution of the Schottky anomaly when analyzing the temperature dependences of the heat capacity in a crystal of $GdAl_3(BO_3)_4$. The lower level of the isolated ion Gd^{3+} is the spin multiplet $S_{7/2}$ [11], which weakly interacts with the crystal field. The structure of Gd^{3+} levels was studied by EPR in an yttrium aluminum borate crystal with a gadolinium concentration of 0.2 % [12]. The eightfold degenerate level of the free trivalent gadolinium ion in the trigonal crystal field splits into four closely spaced Kramers doublets. The lower one is the doublet $\pm 1/2$. The levels above are $\pm 3/2$, $\pm 5/2$ and $\pm 7/2$. The corresponding energy differences relative to the ground doublet were found to be 0.13, 0.37, and 0.67 K. With an increase in the gadolinium concentration, a change in the splitting values of the ground multiplet should be expected. In addition, interactions with neighboring ions Gd^{3+} may affect the structure of gadolinium energy levels in the crystal field, as was observed for crystals of rare-earth aluminum garnets [13,14]. To approximate the contribution of the Schottky anomaly in the $GdAl_3(BO_3)_4)$ crystal, we used a simplified approach, considering four equidistant Kramers doublets spaced by Δ, which served as an additional fitting parameter.

The result of approximating the heat capacity of a $GdAl_3(BO_3)_4$ crystal divided by the cube of temperature, taking into account the Debye contribution, two Einstein contributions and the Schottky anomaly, is shown in Figure 2, *a*. This figure also shows individual contributions to the heat capacity. The corresponding fitting parameters are shown in the table. It should be noted that the splitting characteristic of Kramers doublets Δ is close in order of magnitude to the splitting found by EPR in weakly doped yttrium aluminum borate. The Einstein temperatures for $GdAl_3(BO_3)_4$, as expected, were lower than the corresponding temperatures for yttrium aluminum borate. As in the case of the crystal $YAl_3(BO_3)_4$, the approach used provides an excellent match of the theoretical curve for the temperature dependence of the heat capacity over the entire range from 1.9 to 100 K (Figure 1).

In solid solution $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4)$, the phonon spectrum includes translational vibrations of both gadolinium and yttrium ions. Therefore, the maximum on the temperature dependence C/T^3 should be considered as a superposition of Einstein's contributions from two low-frequency optical modes Gd^{3+} and two optical modes Y^{3+}. Moreover, the coefficients r_{E1} and r_{E2} for these contributions should be equal to the coefficients calculated for gadolinium and yttrium aluminum borates multiplied by the relative fractions of ions Gd^{3+} (0.17) and Y^{3+} (0.83) in the composition of the crystal. A similar analysis of the maximum on the curve $C/T^3(T)$ was performed for solid solutions of garnets and aluminates in Ref. [15]. To approximate the contribution of the Schottky anomaly in a solid solution crystal, we used a simplified approach, as in the case of aluminum gadolinium borate, assuming the splitting of an eightfold degenerate gadolinium level into four Kramers doublets equidistant by Δ. The splitting parameter Δ for $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$ turned out to be very close to the values obtained in Ref. [12].

However, the solid solution $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$ is not a fully ordered crystal system, unlike crystals of yttrium and gadolinium aluminum borates. The disorder in the solid solution is related to the statistical distribution of ions Y^{3+} and Gd^{3+} at positions $3a$ in the lattice. In glasses, other amorphous solids, and crystals with elements of disorder, a narrow region of excessive vibrational states occurs at low frequencies, which leads to anomalies in thermal conductivity, heat capacity, and acoustic properties [16]. In disordered solids, an additional maximum appears on the curve $C/T^3(T)$ in the temperature range below 10 K. An increase of C/T^3 of about 7 K is seen in Figure 2, *b* for $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$. This abnormal rise can also be interpreted within the framework of the Einstein model with temperature θ_{exc} and number of modes r_{exc}. Thus, the Debye contribution, the Einstein contributions due to low-frequency optical modes, the Schottky anomaly, and the contribution of excess oscillatory states should be taken into account when analyzing the heat capacity in a solid solution crystal $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$.

An approximation of the temperature dependence C/T^3 for a solid solution is shown in Figure 2, *b*, which also shows all the individual contributions. The set of fitting parameters is shown in the table. As for the extreme compositions, the approach used provides an excellent approximation of the temperature dependence of the heat capacity over the entire range from 1.9 to 100 K (Figure 1).

4. Conclusion

The measured dependences of heat capacity on temperature in single crystals of yttrium and gadolinium aluminum borates allow for an interpretation that takes into account the phonon contributions of Debye and Einstein and Schottky anomalies associated with spin level splitting Gd^{3+}. It is shown that the revealed maxima in the $C/T^3(T)$ dependence are due to low-frequency optical vibrations of Y^{3+} or Gd^{3+} ions, characteristic of the $R32$ symmetry. When interpreting the heat capacity in a solid solution $Y_{0.83}Gd_{0.17}Al_3(BO_3)_4$), the contribution of low-frequency optical vibrations was considered as a superposition of the contributions of vibrations of yttrium and gadolinium ions. An abnormal increase in the heat capacity in the solid solution single crystal near 7 K was interpreted as the result of the existence of excessive vibrational states resulting from the disorder of substitution of Y^{3+} and Gd^{3+} over positions $3a$ in the crystal lattice, similar to the features of the density of vibrational states in amorphous solids. The agreement of the experiment and the theoretical approximation is observed in the range from 1.9 to 100 K for all three samples of aluminum borates.

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Conflict of interest

The authors declare that they have no conflict of interest.

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