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SPECIFIC HEAT OF $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, AND $GdFe_3(BO_3)_4$

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The specific heat was measured in the range 0.4–300 K in $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, and $GdFe_3(BO_3)_4$ single crystals. Sharp anomalies were found at temperatures of first-order structural, second-order antiferromagnetic, and first-order spin-reorientational transitions. The Neel temperature of about 37 K was found to be virtually independent of presence of rare-earth ions, indicating rather weak coupling of Gd and Fe subsystems. The contribution of the magnetic system to specific heat was separated through the scaling procedure allowing determination of the magnetic entropy of Fe and Gd subsystems. At the lowest temperatures, the specific heat in $GdFe_3(BO_3)_4$ exhibits a Schottky-type anomaly, which is due to Gd^{3+} eight-fold degenerate ground level splitting by the internal magnetic field of the Fe subsystem of about 7 T.

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The borates with the general formula $RM_3(BO_3)_4$, where R stands for a rare earth or yttrium and M = Al, Ga, Sc, Cr, Fe, have attracted a considerable attention recently because of their good luminescent and nonlinear optical properties combined with excellent physical parameters and chemical stability. The crystals of $YAl_3(BO_3)_4$ and $GdAl_3(BO_3)_4$ doped with Nd are used for self-frequency doubling and self-frequency summing lasers [1]. The crystals of $NdAl_3(BO_3)_4$ are efficient media for minilasers [2]. In the case of borates with magnetic M = Cr, Fe ions, the applications for Faraday devices are discussed. The crystals of $GdFe_3(BO_3)_4$ have multiferroic features, which presume the coexistence of elastic, magnetic, and ferroelectric order parameters [3]. Most clearly, the coupling of these parameters was observed in the vicinity of spin-reorientational transition at low temperatures [4, 5].

The crystal structure of $RFe_3(BO_3)_4$ belongs to the trigonal system of the $CaMg_3(CO_3)_4$ type, the cell unit contains three formula units [6]. In rare-earth ferroborates, three kinds of coordinations with oxygen are present: RO_6 trigonal prisms, FeO_6 octahedra, and two types of triangular BO_3 groups. The FeO_6 octahedra share edges such that they form helicoidal chains that run parallel to the c axis and are mutually independent. The RO_6 are isolated polyhedra, each of them connects three helicoidal FeO_6 chains. Both BO_3 triangles and RO_6 trigonal prisms connect three FeO_6 chains.

The structural and magnetic properties of rare-earth ferroborates have become the subject of numerous studies [4, 5, 7–10]. In particular, the heat capacity of $RFe_3(BO_3)_4$ (R = Y, La–Nd, Sm–Ho) pellet samples was measured in [7]. At low temperature, the Fe subsystem in $RFe_3(BO_3)_4$ is antiferromagnetically ordered, while the rare-earth subsystem remains disordered. At high temperature, structural phase transitions occur in $RFe_3(BO_3)_4$ compounds with R = Y, Eu-Ho. While the temperatures of the structural phase transition in $GdFe_3(BO_3)_4$ ($\sim$ 156 K) and $YFe_3(BO_3)_4$ ($\sim$ 445 K) differ significantly, their antiferromagnetic phase transition temperatures coincide ($\sim$ 37 K). The $GdFe_3(BO_3)_4$ compound has a unique feature that dis-

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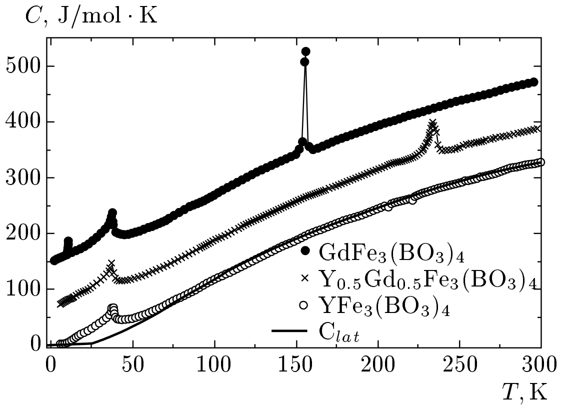

Fig. 1. Temperature dependences of the specific heat in $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, and $GdFe_3(BO_3)_4$. The individual curves are shifted with respect to each other by 75 J/mol K. The lattice contribution C_{lat} in $YFe_3(BO_3)_4$ is shown by the solid line

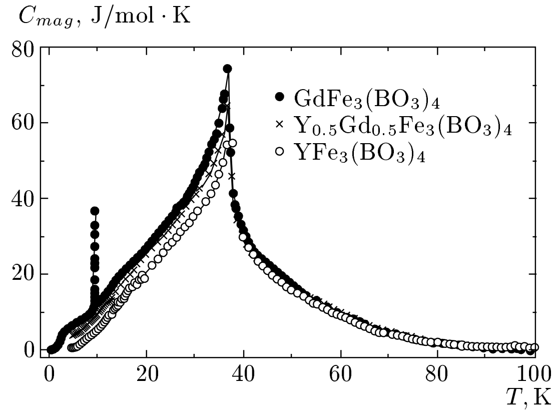

Fig. 2. Temperature dependences of the magnetic specific heat C_{mag} in $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, and $GdFe_3(BO_3)_4$

tinguishes it from any other rare-earth ferroborate. At 9 K, it experiences a spin-reorientational transition, the Fe moments being oriented in the ab plane above this temperature and aligned with the c axis below this temperature [8].

In the present work, we report on specific heat in $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ and $GdFe_3(BO_3)_4$ single crystals. While the C vs. T dependence in $YFe_3(BO_3)_4$ practically reproduces that measured in Ref. [7], the C vs. T dependences in $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ and $GdFe_3(BO_3)_4$ show new important features missed in previous studies.

Single crystals of $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ and $GdFe_3(BO_3)_4$ were grown using a $Bi_2Mo_3O_{12}$-based flux [9]. The seeds were obtained by spontaneous nucleation from the same flux. Transparent single crystals of these ferroborates were green in color and had good optical quality. The specific heat in the range 5–300 K was measured by «Termis» relaxation-type microcalorimeter. At lowest temperatures, the specific heat measurements were performed using a relaxation technique by a commercial heat capacity measuring system PPMS «Quantum Design». In the range of overlap, the results obtained by two techniques coincide within resolution limits.

The temperature dependences of specific heat $C(T)$ in $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, and $GdFe_3(BO_3)_4$ are shown in Fig. 1. Sharp singularities at 156 K in $GdFe_3(BO_3)_4$ and at 234 K in $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ indicate first-order phase transitions. The λ-type peaks at 37 K seen in every sample correspond to a second-order phase transition. Besides these two anomalies, a very narrow peak manifesting a first-order phase transition at 9 K and Schottky-type anomaly at lower temperature are seen in the $GdFe_3(BO_3)_4$ compound.

The λ-type singularity at 37 K in the $C(T)$ dependence in $YFe_3(BO_3)_4$ corresponds to antiferromagnetic ordering of the iron subsystem. The magnetic measurements [9] have shown that at high temperatures, the magnetic susceptibility of $YFe_3(BO_3)_4$ obeys the Curie–Weiss law with the effective magnetic moment corresponding to the spin $s = 5/2$ of Fe^{3+} ions. Assuming that the total magnetic entropy of the iron subsystem $S_{mag} = 3R\ln(2s+1) = 44.7$ J/mol K (where $R = 8.31$ J/mol K is the gas constant) is released at antiferromagnetic ordering, the lattice contribution to the overall specific heat is fitted by the sum of the Debye function (dominating at low temperatures) and four Einstein functions. This fit is shown by the solid line in Fig. 1.

Subtraction of the lattice contribution C_{lat} from the overall specific heat in $YFe_3(BO_3)_4$ has allowed determining the temperature dependence of the magnetic specific heat C_{mag}, shown in Fig. 2. The temperature dependence of the magnetic entropy in $YFe_3(BO_3)_4$,

$$S_{mag} = \int_0^T \frac{C_{mag}}{T}\,dT,$$

is shown in Fig. 3. It saturates well above the Neel temperature, indicating that a significant part of the magnetic entropy is released through short-range magnetic correlations in FeO_6 chains.

In $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, a singularity at 234 K in the $C(T)$ dependence corresponds assumingly to a

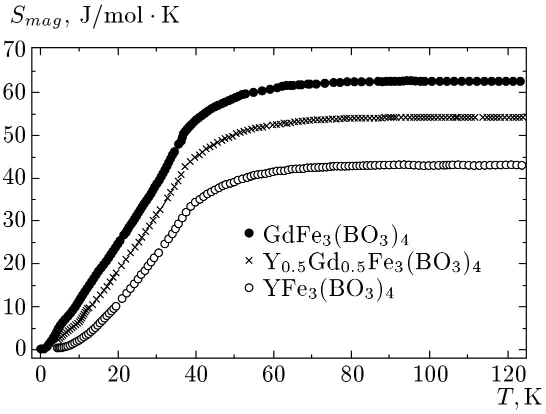

Fig. 3. Temperature dependences of the magnetic entropy in $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, and $GdFe_3(BO_3)_4$

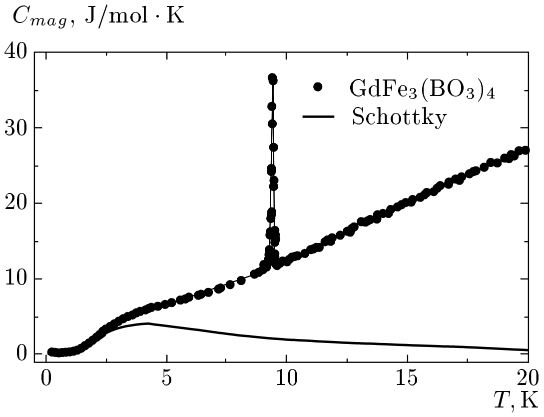

Fig. 4. Temperature dependences of the magnetic specific heat in $GdFe_3(BO_3)_4$. The solid line represents the Schottky-type contribution to the specific heat

structural phase transition. This assumption is based on the fact that the temperature of this transition is located between the temperatures of structural phase transitions in $YFe_3(BO_3)_4$ (445 K) and $GdFe_3(BO_3)_4$ (156 K). Compared with a sharp anomaly at the structural phase transition in $GdFe_3(BO_3)_4$, the singularity in $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ is broadened due to stochastic distribution of yttrium and gadolinium ions in the structure. These ions have slightly different radii, which leads to local distortions of the crystal lattice.

To subtract C_{mag} from the overall specific heat in $GdFe_3(BO_3)_4$ and $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, it is necessary to estimate the lattice contribution C_{lat} correctly. In the paramagnetic state, just this contribution represents the overall specific heat. To estimate C_{lat} in $GdFe_3(BO_3)_4$ and $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, the lattice contribution defined in $YFe_3(BO_3)_4$ can be used through a special scaling procedure. This procedure is based on the assumption that the lattice part of the heat capacity of isostructural compounds can be expressed by a common function whose argument is T/Θ, where Θ is the Debye temperature. For two compounds, 1 and 2, it follows that $C_1(T_1/\Theta_1) = C_2(T_2/\Theta_2)$, and therefore $T_1/T_2 = \Theta_1/\Theta_2 = r$. Because the phonon spectra of isostructural compounds are not strictly identical, the ratio r is not a constant but slightly depends on temperature. For example, in case of $CdFe_3(BO_3)_4$ the scaling parameter is $r = 1.0525 - 5.1786 \cdot 10^{-4}T + 2.5324 \cdot 10^{-6}T^2$, meaning that the Debye temperature in $CdFe_3(BO_3)_4$ is approximately 5 % lower than that in $YFe_3(BO_3)_4$. The scaling procedure employed puts into correspondence the temperatures where the specific heat of $GdFe_3(BO_3)_4$ or $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ equals C_{lat} in $YFe_3(BO_3)_4$. Therefore, the temperature dependence of C_{lat} in $YFe_3(BO_3)_4$ as a function of (rT) represents the lattice contribution of $GdFe_3(BO_3)_4$ or $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$.

The temperature dependences of the magnetic contribution C_{mag} and magnetic entropy S_{mag} in $GdFe_3(BO_3)_4$ and $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ are shown in Figs. 2 and 3. In $GdFe_3(BO_3)_4$, S_{mag} saturates at 62 J/mol K, in correspondence with the magnetic entropy released in both iron (44.7 J/mol K) and gadolinium (17.2 J/mol K) subsystems $S_{mag} = S_{\mathrm{Gd}} + S_{\mathrm{Fe}} = R\ln(2\times 7/2+1) + 3R\ln(2\times 5/2+1)$. In $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, S_{mag} saturates at 53 J/mol K due to reduction of the entropy released in the rare-earth subsystem, in this case $S_{\mathrm{Gd}} = 0.5R\ln(2\times 7/2+1) = 8.6$ J/mol K. The observation of excessive magnetic entropy in $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$ as compared with that in $YFe_3(BO_3)_4$ does not signal the ordering in the rare-earth subsystem, however. The fact that the Neel temperature in $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, and $GdFe_3(BO_3)_4$ is insensitive to the substitution of nonmagnetic yttrium for gadolinium indicates that the Gd–O–Fe superexchange is not important for the formation of the Neel order. Instead, the Gd subsystem becomes fully polarized by the magnetically ordered Fe subsystem.

In addition to the structural phase transition at 156 K and antiferromagnetic phase transition at 37 K, a very sharp peak at 9 K is seen in $GdFe_3(BO_3)_4$. The magnetic part of the specific heat in this compound is shown in Fig. 4. This peak corresponds to spin reorientation in the iron subsystem, which is confirmed by magnetization measurements [8, 10].

At lowest temperatures, the $C(T)$ curve in $GdFe_3(BO_3)_4$ exhibits a Schottky-type anomaly, which can be attributed to splitting of eight-fold degenerate levels of Gd^{3+} in an internal magnetic field of the iron subsystem. This Zeeman splitting amounts to approximately 10 K, which corresponds to the internal magnetic field about 7 T. The temperature dependence of specific heat due to the Schottky anomaly is shown in Fig. 4 by the solid line.

In summary, we studied the specific heat in a series of isostructural compounds $YFe_3(BO_3)_4$, $Y_{0.5}Gd_{0.5}Fe_3(BO_3)_4$, and $GdFe_3(BO_3)_4$, which differ by the content of rare-earth elements. The magnetic entropy released at this ordering contains parts related to the iron and gadolinium subsystems. The respective contributions differ, however, in a sense that the exchange-coupled Fe^{3+} subsystem becomes ordered, while that of fully polarized Gd^{3+} remains paramagnetic. The influence of the gadolinium subsystem on physical properties of these ferroborates is seen in a drastic reduction of the structural phase transition temperature in substituting Y for Gd. In $GdFe_3(BO_3)_4$ another unique feature is observed at 9 K, a spin reorientation in Fe subsystem. At low temperatures, the Schottky-type anomaly in specific heat has allowed estimating the internal magnetic field in $GdFe_3(BO_3)_4$.

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