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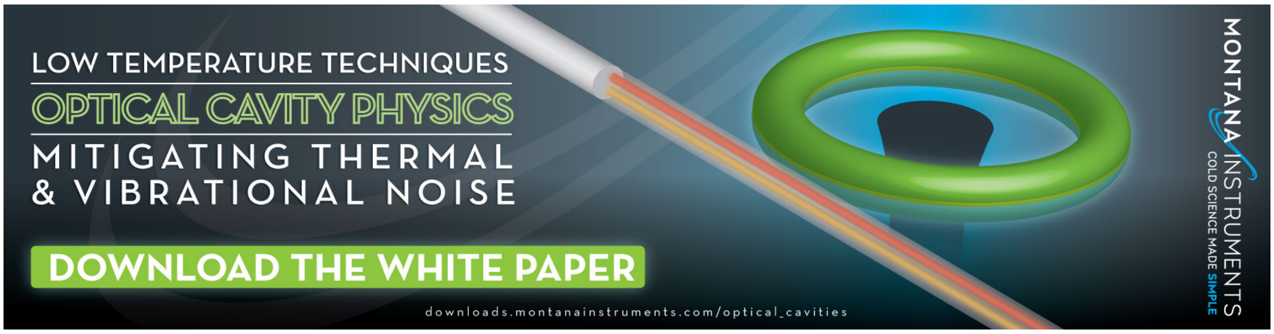
V. A. Bedarev, M. I. Paschenko, M. I. Kobets, K. G. Dergachev, E. N. Khatsko, S. L. Gnatchenko, A. A. Zvyagin, T. Zajarniuk, A. Szewczyk, M. U. Gutowska, L. N. Bezmaternykh, and V. L. Temerov



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V. A. Bedarev,[a] M. I. Paschenko, M. I. Kobets, K. G. Dergachev, E. N. Khatsko,
S. L. Gnatchenko, and A. A. Zvyagin

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Lenin Ave., Kharkov 61103, Ukraine

T. Zajarniuk, A. Szewczyk, and M. U. Gutowska

Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

L. N. Bezmaternykh and V. L. Temerov

L.V. Kirenskii Institute of Physics, Siberian Branch of the Russian Academy of Sciences, Krasnoyarsk 660036, Russia

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Magnetic ordering temperature, initial splitting and effective *g*-factor of the ground quasi-doublet of a Tb^{3+} ion were determined by investigating the heat capacity and ESR in a $TbAl_3(BO_3)_4$ single crystal. The parameters of the magnetic interaction were calculated. *© 2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4927082]

1. Introduction

Trigonal rare-earth aluminum borates $RAl_3(BO_3)_4$ (R is the rare-earth element) exhibit well-pronounced fluorescent and nonlinear optical properties which enable application of these materials for designing efficient mini-lasers as well as other electro-optical devices of new generation.[1] Moreover, the giant magnetoelectric effect has been recently discovered in these materials.[2–4]

No magnetic ordering has been observed in aluminum borates, possibly due to the fact that the studies of the magnetic properties of these compounds have been carried out at temperatures above 2 K.[5] Typically, a magnetic ordering in rare-earth compounds occurs at rather low temperatures (about 1 K).[6] Specific features and diversity of the magnetic properties of these compounds are determined by the peculiarities of the electronic structure of the rare-earth ions and the crystal fields of the ligands.[6]

In aluminum borate $TbAl_3(BO_3)_4$, the symmetry of the positions of Tb^{3+} ions is described by the trigonal point group D_3.[7] The crystal field of this symmetry splits the $^7F_6$ ground multiplet of a Tb^{3+} ion into 5 singlets and 4 doublets.

The study of the transmission spectra of a $TbAl_3(BO_3)_4$ crystal in the optical range suggests that the ground state of a Tb^{3+} ion constitutes of two closely located singlet levels, a quasidoublet.[7] The energy interval between the ground quasidoublet and the first excited state is about 200 cm^{-1}.[7] Terbium ions possess a significant magnetic moment, so it is expected that the dipole-dipole interaction plays a decisive role in the magnetic ordering. In terbium aluminum borate, both ferromagnetic and antiferromagnetic ordering are possible. Knowing the magnetic ordering temperature T_c and the initial quasidoublet splitting Δ, we can determine the molecular field constant λ_0 in the case of ferromagnetic ordering and the effective field constants for the intra-sublattice $\lambda_{11} = \lambda_0$ and inter-sublattice λ_{12} interactions in the case of antiferromagnetic ordering.[8,9]

In the present work, a study of the specific heat and the ESR was carried out with aim to determine the magnetic interaction parameters in a $TbAl_3(BO_3)_4$ crystal.

2. Experimental technique

For resonance measurements, a single-crystal plate of 1.5 × 1.5 mm, 1 mm thick was cut. Specific heat measurements were carried out on a sample of a smaller volume: 1.5 × 1.5 mm, 0.1 mm thick. The trigonal *c* axis was perpendicular to the plane of the plates.

Specific heat was measured by the relaxation method using a Physical Property Measurement System (PPMS, Quantum Design).

For resonance measurements in the frequency range of 18–142 GHz, a direct amplification spectrometer was used. The polarization of the microwave field was perpendicular to the trigonal axis of the crystal. The dc magnetic field was produced by a superconducting solenoid and applied along the *c* axis with an accuracy of 0.5°.

3. Experimental results

Fig. 1 shows the temperature dependence of the specific heat of $TbAl_3(BO_3)_4$. It is seen that at $T_c = 0.68$ there is a feature in the temperature dependence of the specific heat, which is characteristic of a phase transition of the second kind. This feature can be attributed to a phase transition to a magnetically ordered state. As the temperature is lowered below 0.3 K, an increase in heat capacity, apparently due to the nuclear contribution, is observed.

Knowing the magnetic ordering temperature, the initial splitting of the quasidoublet and the *g*-factor of a Tb^{3+} ion can be determined by the ESR technique in the paramagnetic region. The experimental temperature of 4.2 K was selected since a line broadening due to spin-lattice relaxation processes occurs at higher temperatures. At lower temperatures, there is a critical region preceding the magnetic

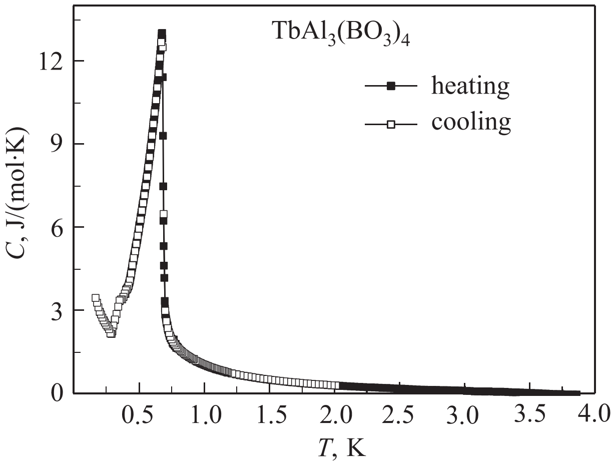

FIG. 1. Temperature dependence of the specific heat of a TbAl$_3$(BO$_3$)$_4$ single crystal at $H = 0$.

ordering temperature, where an ESR line broadening occurs as well.

In our experiment, the electron spin resonance of a Tb^{3+} ion in a TbAl$_3$(BO$_3$)$_4$ crystal may be due to the transitions between the components of the lowest quasidoublet since the distance to the next excited level is about 200 cm^{-1}. Thus, the ESR spectrum of a Tb^{3+} ion should consist of a single line.

Fig. 2 shows, as an example, the ESR spectra of a TbAl$_3$(BO$_3$)$_4$ crystal in a magnetic field **H** || c at different frequencies at a temperature of 4.2 K. As is seen in the spectra, there is no absorption at a frequency of 26.01 GHz, while at a frequency of 29.04 GHz an absorption line is observed. Increasing the frequency to 73.12 GHz and then to 104.8 GHz leads to a shift of the absorption line into the region of higher magnetic fields.

4. Discussion

Based on the obtained experimental data, we plotted the frequency-field dependence $\nu(H)$ of the absorption lines in the ESR spectrum of terbium alumoborate at $T = 4.2$ K, which is shown in Fig. 3. Let us determine the initial splitting Δ and the effective g-factor of the line. The experimental dependence $\nu(H)$ is well described by the expression

$$\nu(H) = \sqrt{\Delta^2 + g_{\mathrm{eff}}{}^2\mu_B{}^2H^2}, \tag{1}$$

with the initial splitting $\Delta \approx (27.8 \pm 1.5)$ GHz ($\approx(0.91 \pm 0.05)$ cm^{-1}) and the effective g-factor ≈ 16.1.

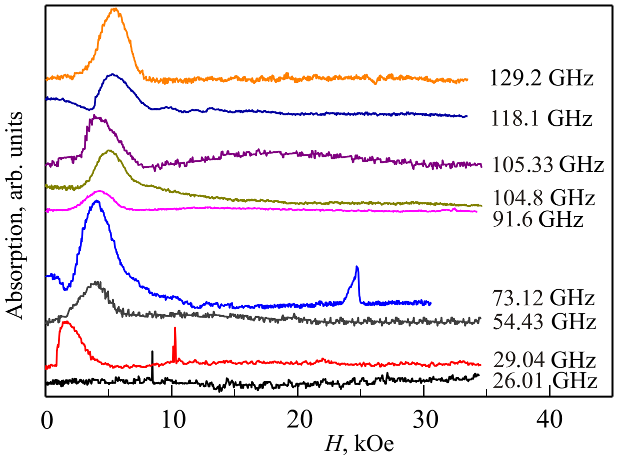

FIG. 2. ESR spectrum of a TbAl$_3$(BO$_3$)$_4$ crystal in a magnetic field **H** || c at different frequencies and a temperature of 4.2 K.

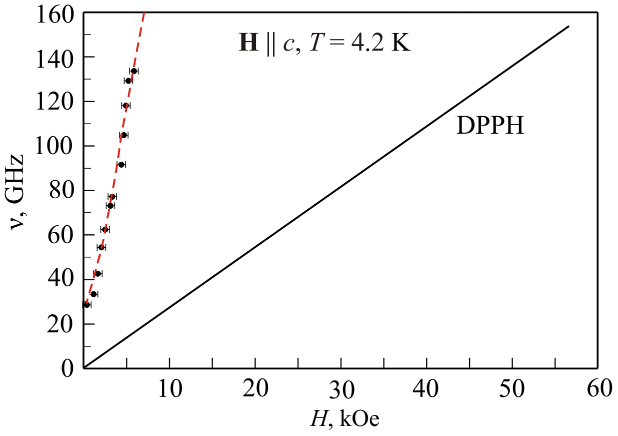

FIG. 3. Frequency-field dependence of the absorption lines of the ESR spectrum of a TbAl$_3$(BO$_3$)$_4$ crystal in a magnetic field **H** || c at a temperature of 4.2 K. The experimental data are shown with solid circles, the extrapolation is shown as a dashed line, and the solid line represents the frequency-field dependence for the reference signal of diphenylpicrylhydrazyl (DPPH).

Let us discuss the obtained results in the framework of the molecular field theory for a singlet ordered magnet.[8] This will, in particular, allow us to estimate the magnitude of the ion-ion magnetic interaction in terbium aluminum borate. In the molecular-field approximation in the absence of an external magnetic field, the equation for the specific heat of the magnetic subsystem of a singlet two-sublattice antiferromagnet has the form (for a singlet ferromagnet, the following equation has the same form but with $\lambda_{12} = 0$ and the antiferromagnetic order parameter l replaced with the ferromagnetic order parameter m):

$$C = T\frac{\partial^2 a}{\partial T^2}\tanh\frac{a}{2T} + \frac{\left(\dfrac{\partial a}{\partial T} - \dfrac{a}{T}\right)^2}{\cosh^2(a/T)}, \tag{2}$$

where $a = [(\Delta/2)^2 + (g_{eff}\mu_B)^2(\lambda_{11} - \lambda_{12})l^2]^{1/2}$ and l is the antiferromagnetic order parameter (antiferromagnetic vector). The Boltzmann constant is set equal to unity $k_B = 1$ (i.e., in what follows, all the energy values are expressed in degrees Kelvin). At temperatures above the critical temperature $T \geq T_c$, $l = 0$ and thus, the specific heat is determined by the equation $C = \Delta^2/4T^2\cosh^2(\Delta/2T)$. Therefore, the heat capacity of the non-interacting effective spins of terbium ions should exhibit a maximum in the temperature dependence, associated with the Schottky anomaly. On the other hand, for $T < T_c$, the order parameter is found by solving the self-consistency equation $\tanh(a/T) = a/(g_{eff}\mu_B)^2(\lambda_{11} - \lambda_{12})$. From the solution of the self-consistency equation, it follows that, in particular, $T_c = (\Delta/2)\mathrm{arctanh}[\Delta/(g_{eff}\mu_B)^2(\lambda_{11} - \lambda_{12})]$. Below the ordering temperature, the expression for the specific heat of the magnetic subsystem has the form

$$C = \frac{\Delta}{4T^2\tanh^2\left(\frac{\Delta}{2T}\right)}\,\frac{1}{l^2+\tanh^2\left(\frac{\Delta}{2T}\right)}\left\{\left[1-l^2-\tanh^2\left(\frac{\Delta}{2T}\right)\right]\left[Tl\frac{\partial l}{\partial T}-l^2-\tanh^2\left(\frac{\Delta}{2T}\right)\right]^2 + \frac{2T^3}{\Delta}\tanh\left(\frac{\Delta}{2T}\right)\left[\left(\frac{\partial l}{\partial T}\right)^2\tanh\left(\frac{\Delta}{2T}\right)+l\left(l^2+\tanh^2\left(\frac{\Delta}{2T}\right)\right)\frac{\partial^2 l}{\partial T^2}\right]\right\}. \tag{3}$$

The specific heat contains contributions from the Schottky anomaly and the peak (peculiarity) in the temperature dependence, associated with magnetic ordering. When $T \to T_c$ from high temperatures, the heat capacity of the magnetic subsystem is equal to $C = \Delta^2/4T_c^2\cosh^2(\Delta/2T_c)$. At low temperatures, the expression for the specific heat has the form

$$C = \frac{\Delta^2}{4T_c^2\cosh^2(\Delta/2T_c)}\,\frac{2T}{\Delta\tanh(\Delta/T_c)}\left[(f'_0)^2\tanh\left(\frac{\Delta}{T_c}\right)+f''_0\right].$$

Here, it is taken into consideration that the solution of the self-consistency equation for the order parameter l has the form $l\cosh^2(\Delta/2T_c) = f(1-T/T_c)$, and the index 0 denotes that f' and f'' are taken at $T=0$. It can be seen that the molecular field theory for an ordered singlet magnet, oddly enough, qualitatively correctly describes the behavior of the low-temperature heat capacity of terbium aluminum borate (see Fig. 1). Typically, the molecular field theory does not predict correctly the low-temperature behavior of the heat capacity in the magnetically ordered phase. In such a phase, the major contribution to the magnetic specific heat is due to the spin waves ($C \sim T^{3/2}$ for a ferromagnet and $C \sim T^3$ for an antiferromagnet). However, in the case of terbium aluminum borate, the spin waves appear to have a gap in the spectrum, and therefore, their contribution to the heat capacity is exponentially small. Knowing the size of the gap determined from the ESR data, $\Delta \approx 0.9\,\mathrm{cm}^{-1} \approx 1.3\,\mathrm{K}$, it can be estimated that the heat capacity maximum corresponding to the Schottky anomaly should be observed at $T \approx 0.4\,\mathrm{K}$. The "tail" of this anomaly was indeed registered in the pretransition region of the temperature dependence of the specific heat (see Fig. 1). On the other hand, using the values of Δ, the effective g-factor and the magnetic ordering temperature T_c, we can determine the magnitude of the effective interaction between the magnetic moments of terbium ions:

$$\lambda_{11} - \lambda_{12} = \Delta/2(g_{\mathrm{eff}}\mu_B)^2\tanh(\Delta/2T_c)$$

(in the case of ferromagnetic ordering, we assume $\lambda_{12} = 0$). Substituting in the equation $\Delta \approx 1.3\,\mathrm{K}$, $g = 16.1$, $\mu_B = 0.335\,\mathrm{K/T}$, and $T_c = 0.68\,\mathrm{K}$, we obtain the values of $(\lambda_{11} - \lambda_{12})$ and $\lambda_{11} = \lambda_0$ equal to $0.03\,\mathrm{T^2/K}$.

In conclusion, the study of low-temperature behavior of the specific heat allowed us to determine the magnetic ordering temperature of the rare-earth subsystem of $\mathrm{TbAl_3(BO_3)_4}$, while the ESR experiments provided the initial splitting Δ and the effective g-factor of the lowest quasidoublet of a Tb^{3+} ion. It was shown that the molecular field theory describes quite well the low-temperature behavior of the specific heat of terbium aluminum borate. The low temperature of the magnetic ordering and, therefore, a low magnitude of the effective magnetic interparticle interaction leads to the assumption about the dipole-dipole nature of magnetic ordering in this compound (the estimates of the magnetic dipole interaction between the terbium ions are in order-of-magnitude agreement with the above estimate for the effective interparticle magnetic interaction).

However, the currently available data are insufficient to determine the nature of the magnetic ordering (ferromagnetic or antiferromagnetic) in terbium aluminum borate. This requires measurements of the magnetic characteristics of the crystal below the ordering temperature.

[a]Email: bedarev@ilt.kharkov.ua

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