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journal homepage: www.elsevier.com/locate/jmmmThe Faraday effect in $\text{TbFe}_3(\text{BO}_3)_4$ and $\text{TbAl}_3(\text{BO}_3)_4$ boratesV.A. Bedarev^a, M.I. Pashchenko^{a,*}, D.N. Merenkov^a, Yu.O. Savina^a, V.O. Pashchenko^a, S.L. Gnatchenko^a, L.N. Bezmaternykh^b, V.L. Temerov^b^a B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, 47 Lenin Ave., Kharkov 61103, Ukraine^b L.V. Kirenskii Institute of Physics, Siberian Branch of the Russian Academy of Sciences, Krasnoyarsk 660036, Russia

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ABSTRACT

The magnetic field dependences of the Faraday rotation of light and the magnetization of antiferromagnet $\text{TbFe}_3(\text{BO}_3)_4$ and paramagnet $\text{TbAl}_3(\text{BO}_3)_4$ compounds have been investigated. It is established that the main contribution to the Faraday rotation in the $\text{TbFe}_3(\text{BO}_3)_4$ is associated with the Tb^{3+} subsystem at low temperatures. The antiferromagnetic ordering effects on this contribution is shown.

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1. Introduction

Recently the multiferroic materials have received much attention among researchers due to their unusual properties. The multiferroic materials exhibit several types of long range magnetic ordering, spontaneous electric polarization and/or ferroelasticity. A new class of such materials is compounds with a general formula $\text{RM}_3(\text{BO}_3)_4$, where R is a rare earth element and $\text{M}=\text{Al}$, Ga, Sc, Cr, and Fe [1–4]. All representatives of this family crystallize in a trigonal system with the space group $R\bar{3}2$. The subfamily of aluminum borates $\text{RAl}_3(\text{BO}_3)_4$, which are paramagnets down to low temperatures, shows the most pronounced multiferroic properties. For example, the crystals $\text{TmAl}_3(\text{BO}_3)_4$ and $\text{HoAl}_3(\text{BO}_3)_4$ have a significant electric polarization in external magnetic fields [3,4]. The magnetic behavior of rare-earth borates changes significantly with the replacement of Al by Fe in $\text{RM}_3(\text{BO}_3)_4$. The interaction between the rare-earth and iron subsystems gives rise to a great variety of different magnetic phases, including incommensurate magnetic structures [5]. In the iron borates, such as $\text{GdFe}_3(\text{BO}_3)_4$ and $\text{TbFe}_3(\text{BO}_3)_4$, the first order structural phase transitions from high symmetry $R\bar{3}2$ to low symmetry space group $P3_121$ were observed at temperatures 192 and 156 K, respectively [6,7]. In the iron borates the Fe subsystem orders antiferromagnetically at low temperatures ($T_N=20\text{--}40$ K) [8]. At the same time the rare-earth subsystem remains paramagnetic below T_N . The magnetic moments of the rare-earth ions are polarized by the exchange coupling between the rare-earth and iron subsystems. Two types of magnetic anisotropy of the antiferromagnetically

ordered state could be observed in the iron borates: the “easy plane” anisotropy for the compounds with Y, Nd, Er, and Tm and the “easy axis” one with Tb, Pr and Dy. The rare-earth iron borates with the “easy axis” anisotropy show spin-flop transitions in magnetic field $H \parallel c$ below T_N [7,9,10].

It is well known that the Faraday rotation angle induced by the external magnetic field is proportional to the magnetization of crystals in both aluminum and iron borates. In the external magnetic field the magnetization $M(H)$ of the $\text{TbFe}_3(\text{BO}_3)_4$ borate can be represented as a sum of the magnetization of the terbium subsystem $M_{\text{Tb}}(H)$ and the magnetization iron subsystem $M_{\text{Fe}}(H)$. For $\text{TbFe}_3(\text{BO}_3)_4$ the rotation angle $\Phi(H)$ in magnetic field $H \parallel c$ can be described by the following expression:

$$\Phi(H) = (AM_{\text{Tb}} + BM_{\text{Fe}})d \quad (1)$$

where A and B are the magneto-optical constants for the terbium and iron subsystems, respectively. d is the thickness of the sample.

In contrast to the terbium iron borate, the crystal $\text{TbAl}_3(\text{BO}_3)_4$ contains only one type of magnetic ions: the terbium subsystem. In external magnetic fields the magnetization $M'(H)$ and the Faraday rotation $\Phi'(H)$ of this crystal are determined by the magnetization of terbium subsystem $M'_{\text{Tb}}(H)$. Therefore, $\Phi'(H)$ for $\text{TbAl}_3(\text{BO}_3)_4$ can be described as follows:

$$\Phi'(H) = A'M'_{\text{Tb}}d \quad (2)$$

where A' is the magneto-optical constant for the terbium subsystem and d is the thickness of the sample.

The study of field dependences of Faraday rotation and magnetization of $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{TbFe}_3(\text{BO}_3)_4$ borates can clarify the contributions of both magnetic subsystems to the Faraday rotation in the crystal $\text{TbFe}_3(\text{BO}_3)_4$ separately, due to the presence of the terbium subsystem as in $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{TbFe}_3(\text{BO}_3)_4$ borates.

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The purposes of the present work are studying of the Faraday effect, determination of the contributions to the Faraday rotation and investigation of the temperature behavior of these contributions in the crystals $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{TbFe}_3(\text{BO}_3)_4$.

2. Experimental results

The single crystal samples of $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{TbFe}_3(\text{BO}_3)_4$ were grown by the method described in [7,11]. For the optical measurements the samples were cut in the form of plane-parallel plates perpendicular to the c -axis. The thickness of the samples was $d=150$ and $110 \mu\text{m}$ for $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{TbFe}_3(\text{BO}_3)_4$, respectively. In order to reduce the elastic stresses after mechanical polishing the samples were annealed at 800°C for 10 h. Both samples have good transparent properties for the visible range of light.

The field dependences of Faraday rotation angle were measured using an experimental system with incorporating modulation and synchronous detection techniques. The sample was maintained in a cold finger of an optical helium cryostat in vacuum. The temperature was controlled by a resistance thermometer to within 0.1 K . A superconducting solenoid with $H_{\text{max}}=55 \text{ kOe}$ was used as a source of magnetic field coinciding with the direction of the light propagation. A filament lamp with interference filter ($\lambda_{\text{max}}=633 \text{ nm}$, $\text{FWHM}=11 \text{ nm}$) was used as a light source.

The field dependences of magnetization of both samples were measured with a Quantum Design SQUID magnetometer MPMS XL5 in the temperature range $8\text{--}35 \text{ K}$ and magnetic fields $0\text{--}50 \text{ kOe}$.

The magnetic field was directed along the c -axis of crystals in both experiments.

2.1. $\text{TbFe}_3(\text{BO}_3)_4$

The magneto-optical properties of $\text{TbFe}_3(\text{BO}_3)_4$ single crystal were measured in an external magnetic field parallel to the c -axis of the crystal. Fig. 1 shows the field dependences of Faraday rotation $\Phi(H)$ in $\text{TbFe}_3(\text{BO}_3)_4$ at fixed temperatures of $8, 10, 15, 20,$ and 35 K . As can be seen in Fig. 1, at the lowest temperature $T=8 \text{ K}$ the curve $\Phi(H)$ has a more pronounced nonlinear character and this nonlinearity gradually diminishes with increasing temperature. At temperature close to $T_N=40 \text{ K}$ the curve $\Phi(H)$ becomes almost linear.

In addition to the optical measurements the magnetic field dependences of magnetization $M(H)$ of the $\text{TbFe}_3(\text{BO}_3)_4$ borate were measured by a SQUID technique. The magnetic experiments were performed at the same temperatures. Fig. 2 shows the field

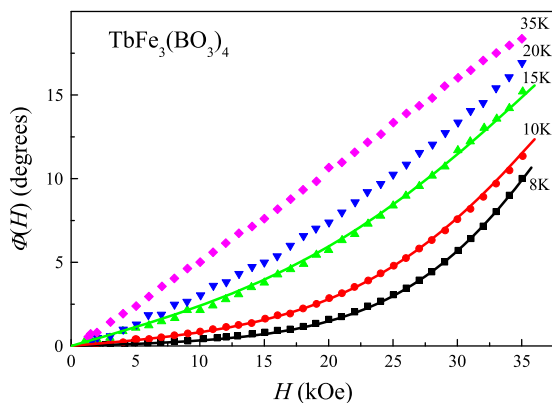


Fig. 1. Field dependences of rotation angle $\phi(H)$ of light polarization plane in the $\text{TbFe}_3(\text{BO}_3)_4$ single crystal at various temperatures for $H \parallel c$. The symbols are the experimental data; the lines are the calculated curves by using expression (1). The thickness of the investigated sample of $\text{TbFe}_3(\text{BO}_3)_4$ is $d=110 \mu\text{m}$.

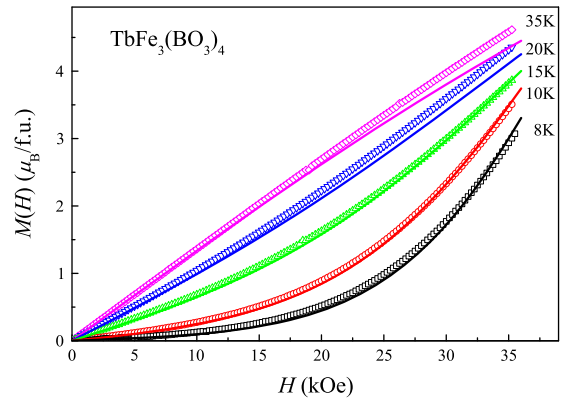


Fig. 2. Field dependences of magnetization $M(H)$ of the $\text{TbFe}_3(\text{BO}_3)_4$ single crystal for $H \parallel c$. Symbols are the experimental data; the lines are the calculated curves by using expression (5).

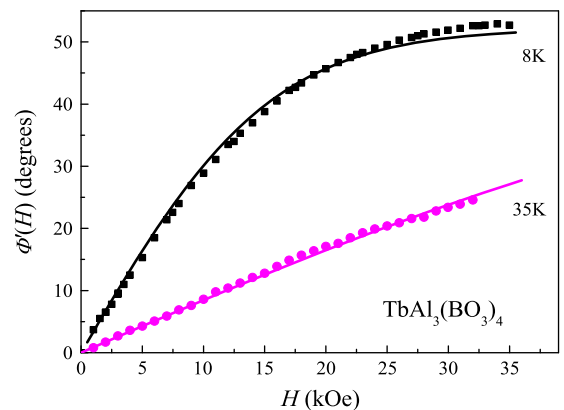


Fig. 3. The field dependence of Faraday rotation of the $\text{TbAl}_3(\text{BO}_3)_4$ single crystal at $T=8$ and 35 K for $H \parallel c$. The symbols are the experimental data; the lines are the calculated curves by using expression (2). The thickness of the investigated sample of $\text{TbAl}_3(\text{BO}_3)_4$ is $d=150 \mu\text{m}$.

dependences of magnetization $M(H)$ of the $\text{TbFe}_3(\text{BO}_3)_4$ borate for magnetic field $H \parallel c$. Evidently, the magnetization curves obtained are very similar to the results of the Faraday rotation experiments. At low temperature the curves $M(H)$ have nonlinear character. At temperatures close to T_N the curves $M(H)$ become almost linear.

2.2. $\text{TbAl}_3(\text{BO}_3)_4$

Further we will consider the magneto-optical properties of $\text{TbAl}_3(\text{BO}_3)_4$ borate which contains a single Tb magnetic subsystem. The optical and magnetic measurements of the $\text{TbAl}_3(\text{BO}_3)_4$ borate were performed under the same experimental conditions as of the $\text{TbFe}_3(\text{BO}_3)_4$ borate. Figs. 3 and 4 show the field dependences of Faraday rotation and magnetization of $\text{TbAl}_3(\text{BO}_3)_4$ at $T=8$ and 35 K and magnetic fields up to 35 kOe for orientation $H \parallel c$. As one would expect the obtained results for magnetization are very similar to the results of the Faraday rotation experiments for $\text{TbAl}_3(\text{BO}_3)_4$. These dependences at $T=8 \text{ K}$ demonstrate that the rotation angle of polarization plane and the magnetization of the $\text{TbAl}_3(\text{BO}_3)_4$ borate tend to a saturation value with increasing magnetic field. Whereas at 35 K the field dependences of Faraday rotation and magnetization do not tend to a saturation and demonstrate almost linear behavior.

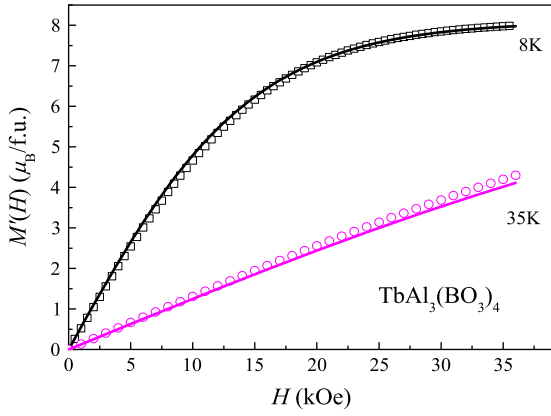


Fig. 4. The field dependence of magnetization of the $\text{TbAl}_3(\text{BO}_3)_4$ single crystal at $T=8$ and 35 K for $H\parallel c$. The symbols are the experimental data; the lines are the calculated curves by using expression (5).

3. Discussion

The magnetic properties of the terbium iron borate are governed by both magnetic subsystems interacting with each other. As mentioned above, the Fe subsystem orders antiferromagnetically with magnetic moments along the c -axis below T_N . The magnetic moments of the Tb subsystem are polarized in the same directions by the field of exchange interaction with the iron subsystem $H_{\text{Tb-Fe}}$. It is known that the ground multiplet of Tb^{3+} ions is 7F_6 ($S=3$, $L=3$, $J=6$). In $\text{TbFe}_3(\text{BO}_3)_4$ this multiplet is splitted into $(2J+1)=13$ Stark levels by the crystal field [12,13]. The ground state of the Tb^{3+} ion is a quasi-doublet, the energy interval between the ground quasi-doublet and the nearest excited states is of the order of 190 cm^{-1} [12,13]. Below T_N the ground quasi-doublet of the Tb^{3+} ions is splitted by the crystal field and exchange field $H_{\text{Tb-Fe}}$. Without the external magnetic field the energy gap between the levels of this quasi-doublet Δ can be determined by the following expression:

$$\Delta = \sqrt{\delta^2 + (g_{\text{eff}}\mu_B H_{\text{Tb-Fe}})^2} \quad (3)$$

where δ is the splitting of the quasi-doublet of Tb^{3+} ions by the crystal field, the value of this splitting is 0.2 cm^{-1} [13], μ_B is the Bohr magneton, and $g_{\text{eff}} \approx 17.5 \pm 0.3$ is the effective g -factor of the ground quasi-doublet [12,13].

The fact that the ground quasi-doublet of the Tb^{3+} ion is well separated from the excited one allows us to use the “quasi-doublet” approximation for estimation of terbium subsystem magnetization at $T < T_N$. Within this approximation the Tb^{3+} system should be divided into two subsystems, each is characterized by the magnetic moment (per formula unit):

$$M_{i\text{Tb}}(H) = \frac{g_{\text{eff}}\mu_B}{4} \tanh\left(\frac{g_{\text{eff}}\mu_B(H \pm H_{\text{Tb-Fe}})}{2kT}\right) \quad (4)$$

where the signs “+” and “−” before exchange field $H_{\text{Tb-Fe}}$ correspond to two antiferromagnetic sublattices of Fe and the subscript $i=1, 2$ specifies the terbium subsystems. This expression does not take into account the splitting of the quasi-doublet by the crystal field δ . The full magnetization (per formula unit) of the terbium subsystem $M_{\text{Tb}}(H) = m_{1\text{Tb}} + m_{2\text{Tb}}$ in a magnetic field $H\parallel c$ will be determined by the following expression:

$$M_{\text{Tb}}(H) = \frac{g_{\text{eff}}\mu_B}{4} \left(\tanh\left(\frac{g_{\text{eff}}\mu_B(H - H_{\text{Tb-Fe}})}{2kT}\right) + \tanh\left(\frac{g_{\text{eff}}\mu_B(H + H_{\text{Tb-Fe}})}{2kT}\right) \right) \quad (5)$$

Table 1

The value of $H_{\text{Tb-Fe}}$ at different temperatures.

T (K)	8	10	15	20	35
$H_{\text{Tb-Fe}}$ (kOe)	39.3	38.4	38	36.14	21

In order to calculate $M_{\text{Tb}}(H)$ at temperatures 8, 10, 15, 20, and 35 K it is necessary to determine the value of $H_{\text{Tb-Fe}}$ at those temperatures. If δ is neglected in expression (3), then exchange field $H_{\text{Tb-Fe}} \approx \Delta/g_{\text{eff}}\mu_B$. Using the temperature dependence of Δ [12], $H_{\text{Tb-Fe}}$ can be estimated for different temperatures. The results of estimation are listed in Table 1.

It is not difficult to calculate the field dependence of $M_{\text{Tb}}(H)$ by (5), and compare it with the experimental dependences $M(H)$ when $H_{\text{Tb-Fe}}$ is already known. As it is shown in Fig. 2, the experimental and calculated curves are in good agreement at 8 K, 10 K and 15 K. But the calculated dependences are deviated from the experimental ones at 20 K and 35 K at magnetic fields higher than 20 kOe. The contribution of iron ion subsystem in the magnetization process is negligible because of the small susceptibility in a magnetic field $H\parallel c$ at low temperatures [14]. However, the iron ion subsystem susceptibility increases with increasing temperature and it begins to contribute to the magnetization of the crystal. Thus, the deviation may be related to the contribution of the iron subsystem $M_{\text{Fe}}(H)$ to magnetization, which increases with the temperature.

As can be seen in Fig. 3, at 8 and 35 K the experimental field dependences of Faraday rotation $\Phi(H)$ in the $\text{TbAl}_3(\text{BO}_3)_4$ borate are in good agreement with the curves calculated by expression (2), where the magneto-optical constant is $A' \approx 430\text{ deg}/(\mu_B/\text{f.u.})\text{ cm}$ for both temperatures.

There is another situation for the $\text{TbFe}_3(\text{BO}_3)_4$ borate. As mentioned above at temperatures 8, 10 and 15 K the magnetization $M(H)$ of this crystal is well described by (5) (Fig. 2). Therefore one can suggest that $M(H) \approx M_{\text{Tb}}(H)$ at those temperatures. One would expect that the field dependences of Faraday rotation are described by (1) without considering the Fe^{3+} subsystem's contribution. As follows from Fig. 1, this assumption is correct. But the magneto-optical constant A is about $300\text{ deg}/(\mu_B/\text{f.u.})\text{ cm}$ for temperatures of 8 and 10 K and about $350\text{ deg}/(\mu_B/\text{f.u.})\text{ cm}$ for 15 K. At temperatures above 15 K the Fe^{3+} subsystem makes a contribution to magnetization of $\text{TbFe}_3(\text{BO}_3)_4$ (Fig. 2). As a consequence, the Faraday rotation in the $\text{TbFe}_3(\text{BO}_3)_4$ borate is determined by both Tb^{3+} and Fe^{3+} subsystems. Since the magneto-optical constants A and B depend on the temperature the contributions from the terbium and iron subsystems to the Faraday rotation in $\text{TbFe}_3(\text{BO}_3)_4$ cannot be separated at temperatures above 15 K. As a consequence the magneto-optical constant B cannot be determined.

Thus at low temperatures the field dependences of Faraday rotation $\Phi(H)$ for the $\text{TbFe}_3(\text{BO}_3)_4$ borate are determined by (1) without considering the Fe^{3+} subsystem contribution. Furthermore, the magneto-optical constants A for $\text{TbFe}_3(\text{BO}_3)_4$ and A' for $\text{TbAl}_3(\text{BO}_3)_4$ are close in the order of magnitude at low temperatures. It allows one to conclude that the Faraday rotation in $\text{TbFe}_3(\text{BO}_3)_4$ is determined by the Tb^{3+} subsystem at low temperatures.

As mentioned above, magneto-optical constants A at 15 K is higher than that at 8 and 10 K. This may be due to the following reason. It is known that the Faraday effect is inversely proportional to the average index of refraction \bar{n} for right- and left-circularly polarized light waves that propagate in a crystal in a magnetic field. Magnetic contribution to the index of refraction \bar{n} will occur at antiferromagnetic ordering in the $\text{TbFe}_3(\text{BO}_3)_4$ crystal [15,16]. Obviously the coefficient A increases with decreasing the magnetic contribution at temperatures approaching to T_N . It should be

noticed that the magneto-optical constant A' for the paramagnet $\text{TbAl}_3(\text{BO}_3)_4$ does not change in the investigated temperature range, in contrast to the antiferromagnet $\text{TbFe}_3(\text{BO}_3)_4$.

4. Conclusion

The magnetic field dependences of the Faraday rotation of light and the magnetization of borates $\text{TbFe}_3(\text{BO}_3)_4$ and $\text{TbAl}_3(\text{BO}_3)_4$ have been investigated. This allows one to make the following conclusions:

1. At low temperature the Faraday rotation in the $\text{TbFe}_3(\text{BO}_3)_4$ borate is determined by the Tb^{3+} subsystem. The magneto-optical constant A for the Tb^{3+} subsystem is about 300 deg/ $(\mu_B/\text{f.u.})$ cm.
2. Magneto-optical constant A depends on the temperature. The temperature evolution of constant A is associated with the antiferromagnetic ordering in the $\text{TbFe}_3(\text{BO}_3)_4$ crystal.
3. In contrast to $\text{TbFe}_3(\text{BO}_3)_4$, the magneto-optical constant A' for the Tb^{3+} subsystem in $\text{TbAl}_3(\text{BO}_3)_4$ borate is temperature independent and is about 430 deg/ $(\mu_B/\text{f.u.})$ cm.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jmmm.2014.03.034>.

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