

Magnetic and Magnetoelectric Properties of Terbium Aluminum Borate

A. M. Kadomtseva^{a,1}, Yu. F. Popov^a, G. P. Vorob'ev^a, A. P. Pyatakov^{a,b}, A. K. Zvezdin^b,
A. A. Mukhin^b, V. Yu. Ivanov^b, L. N. Bezmaternykh^c, I. A. Gudim^c, and V. L. Temerov^c

^aFaculty of Physics, Moscow State University, Moscow, 119992 Russia

^bProkhorov General Physics Institute, Russian Academy of Sciences, Moscow, 119991 Russia

^cKirensky Institute of Physics, Russian Academy of Sciences, Siberian Branch, 660036 Russia

e-mail: mukhin@ran.gpi.ru

Abstract—The magnetic and magnetoelectric properties of terbium aluminum borate are studied. It is established that temperature dependences of the magnetoelectric effects of terbium aluminum borate are analogous to those of terbium ferrobaborate, despite the difference in effective magnetic fields acting on rare-earth ions in these compounds. This confirms the general assumption on the decisive role of the rare-earth element in the magnetoelectric properties of borates.

DOI: 10.3103/S1062873814020142

INTRODUCTION

The discovery of strong magnetoelectric effects in a new class of multiferroics, rare-earth ferrobaborates $RFe_3(BO_3)_4$ [1, 2], stimulated the search for these effects in such isostructural compounds as rare-earth aluminum borates $RAI_3(BO_3)_4$ [3–5], which earlier attracted attention mainly due to their optical and magneto-optical properties [6, 7]. Despite the absence of magnetic ordering, aluminum borates exhibit considerable electric polarization in strong magnetic fields. For example, the magnetic field-induced polarization in holmium aluminum borate exceeds $3000 \mu\text{C}/\text{m}^2$ in a field of ~ 100 kOe [4]. Comparing the magnetoelectric properties of rare-earth aluminum and ferrobaborates is of great interest in understanding magnetoelectric interaction, particularly the role of the rare-earth and iron subsystems and the exchange field between them.

In this work, we measured the magnetic, magnetoelectric, and magnetoelastic properties of terbium aluminum borate. This compound was chosen because it, like terbium ferrobaborate [8], can exhibit considerable magnetoelectric polarization at temperatures up to room temperature, which is of interest in terms of application. It is noteworthy that magnetic field-induced polarization was not observed in earlier studies using this compound [5]. At low temperatures, the uniaxial magnetic anisotropy of a Tb^{3+} ion is indeed large and prevents the emergence of the magnetoelectric properties, but as the population of excited states

grows with temperature, their contribution to the electric polarization increases.

EXPERIMENTAL

$RAI_3(BO_3)_4$ crystals were grown by spontaneous crystallization from a flux. Magnetic measurements were performed on an MPMS-5 magnetic property measurement system (Quantum Design). The magnetoelectric and magnetoelastic properties were investigated in pulse magnetic fields of up to 250 kOe in a temperature range of 4.2–300 K. Magnetostriction was measured using a quartz piezoelectric sensor.

Figure 1 shows the magnetization curves for terbium aluminum borate at $H \parallel c$ and $H \parallel a$; the insert in the figure presents the temperature dependences of susceptibility measured along the same axes in field $H = 1$ kOe. The huge magnetic anisotropy at low temperatures ($\chi_c/\chi_a \sim 400$ at $T = 1.9$ K) testifies to the Ising character of the Tb^{3+} ion. With magnetization along Ising axis c at low temperatures, saturation is reached in fields as low as ~ 20 kOe and the saturation magnetization is $\approx 8 \mu_B/Tb$. In directions perpendicular to axis c , the magnetization is much lower and depends almost linearly on the magnetic field and weakly on the temperature, testifying to its Van Vleck origin; i.e., it is due to the admixing of the excited and ground states of a Tb^{3+} ion in a magnetic field.

Figure 2 shows the field dependences of electric polarization along axis a with magnetization along axis b . As with ferrobaborates, the signs of the longitudinal $\Delta P_a(H_a)$ and transverse $\Delta P_a(H_b)$ effects at the same temperatures are different; this can be explained by analyzing the symmetry of the crystals belonging to the

¹With great sadness we announce that Dr. A.M. Kadomtseva passed away during preparation of this paper.

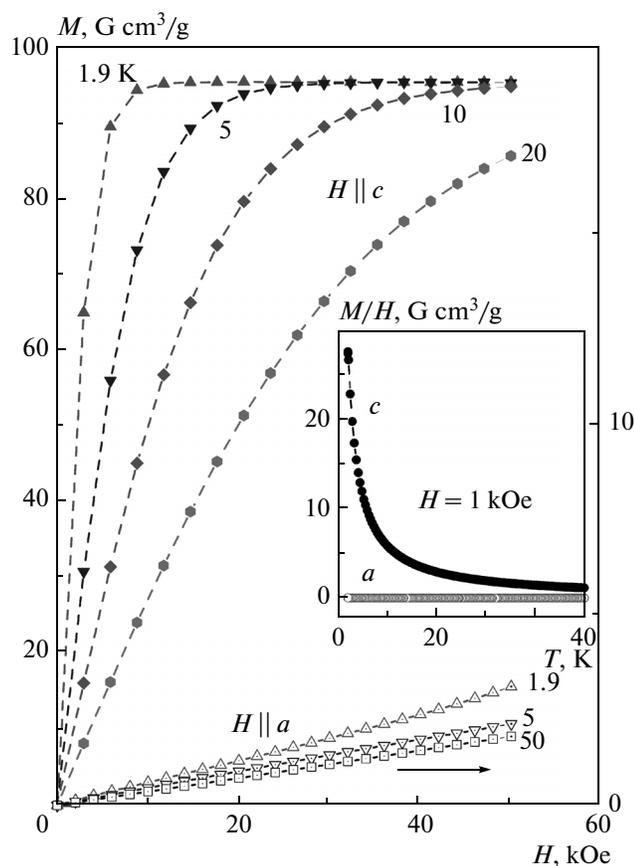


Fig. 1. Magnetization curves for $\text{TbAl}_3(\text{BO}_3)_4$ along the axes c (left scale) and a (right scale). The insert shows the temperature dependence of susceptibility in field $H = 1$ kOe.

space group $R32$ [2]. The magnetoelectric dependences are quadratic, as in other aluminum borates [3–5], but they are nonmonotonically temperature-dependent up to the change in sign. The temperature dependences of polarization along axis a in a field of ~ 100 kOe directed along axes a and b are shown in Fig. 2 by the black triangles. We can see that the magnetic-field-induced polarization has a relatively low but nonzero value at low temperatures; it then changes its sign as the temperature rises and grows to $\sim 25 \mu\text{C}/\text{m}^2$ in the range of temperatures close to room temperature. For comparison, the same figure shows the analogous temperature dependence of magnetoelectric polarization for terbium ferroborate (black dots), which displays similar behavior.

In addition, we measured the temperature dependences of longitudinal magnetostriction $\lambda_a(H_a)$, which were similar and changed their sign as the temperature rose. It should be noted that the magnetostriction was very low ($\sim 10^{-7}$) even in fields of ~ 100 kOe, despite

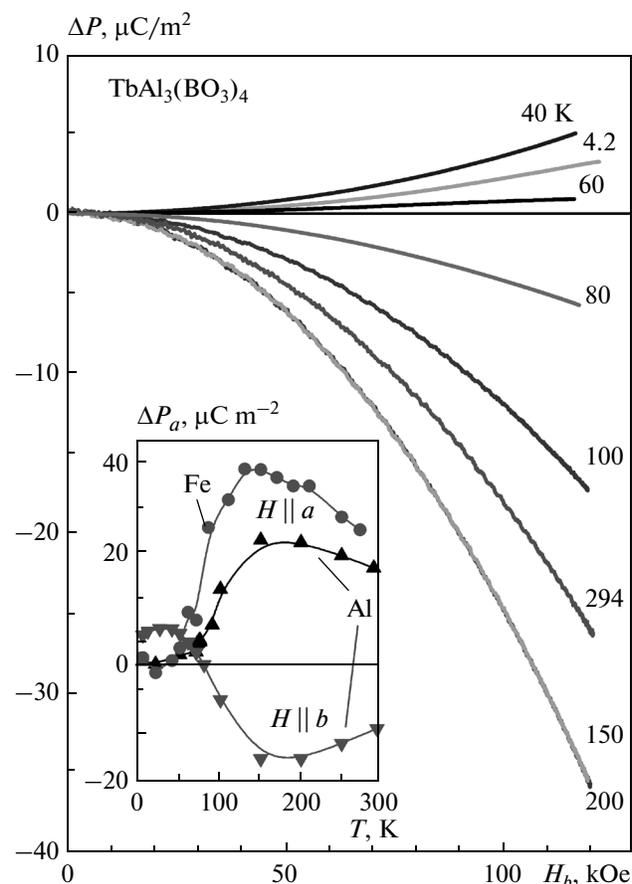


Fig. 2. Field dependences of the electric polarization of $\text{TbAl}_3(\text{BO}_3)_4$, induced along axis a by magnetic field $H \parallel b$ at different temperatures. The insert shows the temperature dependences of P_a for Tb aluminum borate and ferroborate in field $H = 100$ kOe applied along axes a and b .

the growth of the population of excited levels with temperature.

The observed magnetoelectric properties of terbium aluminum borates and ferroborates can be explained by the main contribution to the magnetic field-induced polarization in both classes of compounds coming from Tb^{3+} ions in an external magnetic field and from the R -Fe exchange field in ferroborate. A key role in the formation of the magnetoelectric properties is determined by the strongly anisotropic Ising character of the ground state of a Tb^{3+} ion in a crystal field, which is responsible for the low Van Vleck susceptibility (magnetization) in the basal plane of the crystal and thus the low field-induced polarization. The observed increase in polarization as the temperature rises, accompanied by a change in sign, can be explained by the opposite-signed contribution from excited states of Tb^{3+} ions as their population grows. The characteristic temperatures of 150–200 K, below which the polarization diminishes upon the freezing of these states, correspond to the nearest excited Tb^{3+}

levels in the crystal field, which, according to the optical data for $\text{TbFe}_3(\text{BO}_3)_4$ reported in [9], have an energy of $\sim 200 \text{ cm}^{-1}$. The same features of the ground state of a Tb^{3+} ion also apparently explain the low values of the observed magnetostriction $\lambda_a(H_a)$ and the change in its sign as the temperature rises.

CONCLUSIONS

Terbium aluminum borate and ferroborate with similar Ising characters of the ground states of a Tb^{3+} ion exhibit similar temperature dependences of the magnetoelectric effect, despite the difference in the effective magnetic fields acting on rare-earth ions. This confirms our general assumption about the decisive role of rare-earth elements in the magnetoelectric properties of borates.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, projects nos. 13-02-01093 and 12-02-01261.

REFERENCES

1. Zvezdin, A.K., Krotov, S.S., Kadomtseva, A.M., et al., *JETP Lett.*, 2005, vol. 81, p. 272.
2. Kadomtseva, A.M., Popov, Yu.F., Vorob'ev, G.P., et al., *Low Temp. Phys.*, 2010, vol. 36, no. 6, p. 511.
3. Chaudhury, R.P., et al., *Phys. Rev. B*, 2010, vol. 81, p. 220402(R).
4. Liang, K.-C., et al., *Phys. Rev. B*, 2011, vol. 83, p. 180417(R).
5. Liang, K.-C., et al., *J. Phys.: Conf. Ser.*, 2012, vol. 400, p. 032046.
6. Kellendonk, F. and Blasse, G., *J. Phys. Chem. Solids*, 1982, vol. 43, p. 481.
7. Rubinstein, C.B., et al., *J. Appl. Phys.*, 1964, vol. 35, p. 2338.
8. Zvezdin, A.K., Kadomtseva, A.M., Popov, Yu.F., et al., *JETP*, 2009, vol. 109, no. 1, p. 68.
9. Popova, M.N., Stanislavchuk, T.N., Malkin, B.Z., and Bezmaternykh, L.N., *J. Phys.: Condens. Matter*, 2012, vol. 24, p. 196002.

Translated by E. Bondareva