

Specific Features of Magnetic Properties of $Tb_{1-x}Ho_xAl_3(BO_3)_4$ Aluminoborates

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Abstract—Single crystals $Tb_{1-x}Ho_xAl_3(BO_3)_4$ with $x = 0, 0.1, 0.5, 0.9, 1$ have been grown based on bismuth trimolybdate using a solution–melt method. Their magnetic properties have been studied in the temperature range of 4.2–295 K and magnetic fields to 9 T. The effective magnetic moments $\mu_{\text{eff} \parallel}$ and $\mu_{\text{eff} \perp}$ have been determined. It has been found that the temperature dependence of the susceptibility measured experimentally differs from that calculated on the assumption that the contributions of Tb^{3+} and Ho^{3+} ions are proportional to fractions from the susceptibilities of $TbAl_3(BO_3)_4$ and $HoAl_3(BO_3)_4$, respectively.

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1. INTRODUCTION

In recent years, many domestic and foreign research groups have extensively studied trigonal rare-earth oxyborates $RMe_3(BO_3)_4$ (where $R = Y, La-Lu; Me = Fe, Al, Cr, Ga, \text{ and } Sc$) (e.g., [1–7]). It has been found that borates with two magnetic subsystems (ferroborates $RFe_3(BO_3)_4$) belong to multiferroics [1, 3, 7]. Recently, it was found that aluminoborates $RA_3(BO_3)_4$ that attracted attention mainly due to their optical and magneto-optical properties demonstrate giant magnetoelectric polarization [8–11]. The magnetoelectric polarization in $HoAl_3(BO_3)_4$ at $T = 5$ K in a field of 9 T is $\Delta P_{ab}(B_b) = -5240 \mu C/m^2$ [11], which is highest value for multiferroics and is several times higher than the known maximum values of the magnetoelectric polarization among them in ferroborates.

Anomalous temperature dependence of the magnetoelectric polarization was observed in $TbAl_3(BO_3)_4$. It is related to the increase in the occupancy of upper energy levels of the main multiplet of Tb^{3+} ion with temperature [12].

Despite the large number of experimental and theoretical studies of $RA_3(BO_3)_4$, there is no complete understanding mechanisms of the magnetoelectric interaction in aluminoborates and the role of an R ion in the processes occurring. It was shown in [13] that the difference in the polarizations of $HoAl_3(BO_3)_4$ and $HoFe_3(BO_3)_4$ was mainly due to the difference of the values of the magnetostriction.

It is of a great interest to synthesize and study new aluminoborates of substituted compositions $R1_{1-x}R2_xAl_3(BO_3)_4$ that give much wider variety of observed effects and, it is possible, their amplification. For example, it was revealed in [14] that the maximum polarization of $Ho_{1-x}Nd_xFe_3(BO_3)_4$ is higher than that of $HoFe_3(BO_3)_4$. In [15], the experimental and theoretical studies of the magnetic and magnetoelectric properties of $Ho_{1-x}Nd_xAl_3(BO_3)_4$ made it possible to analyze possible causes of decreasing the magnetic-field-induced polarization and to conclude that the crystal field substantially influence the magnetoelectric properties.

The aim of this work is to synthesize and to experimentally study new substituted aluminoborates $Ho_{1-x}Tb_xAl_3(BO_3)_4$ and to compare their magnetic properties with the magnetic properties of $HoAl_3(BO_3)_4$ and $TbAl_3(BO_3)_4$.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Single crystals $Tb_{1-x}Ho_xAl_3(BO_3)_4$ with $x = 0, 0.1, 0.5, 0.9, 1$ have been grown from a solution–melt 150 g in mass on the basis of bismuth trimolybdate [16]. It is convenient to represent the solution–melt system in quasi-binary form $(100 - n) \text{ wt } \% [Bi_2Mo_3O_{12} + 1.5B_2O_3 + 0.4Li_2MoO_4] + n \text{ wt } \% Ho_{1-x}Tb_xAl_3(BO_3)_4$. For concentration $n = 10 \text{ wt } \%$, the saturation temperature (T_{sat}) was about 985–975°C, and its concentration dependence $dT_{\text{sat}}/dn \approx 30^\circ C \text{ wt } \%$. The crystals

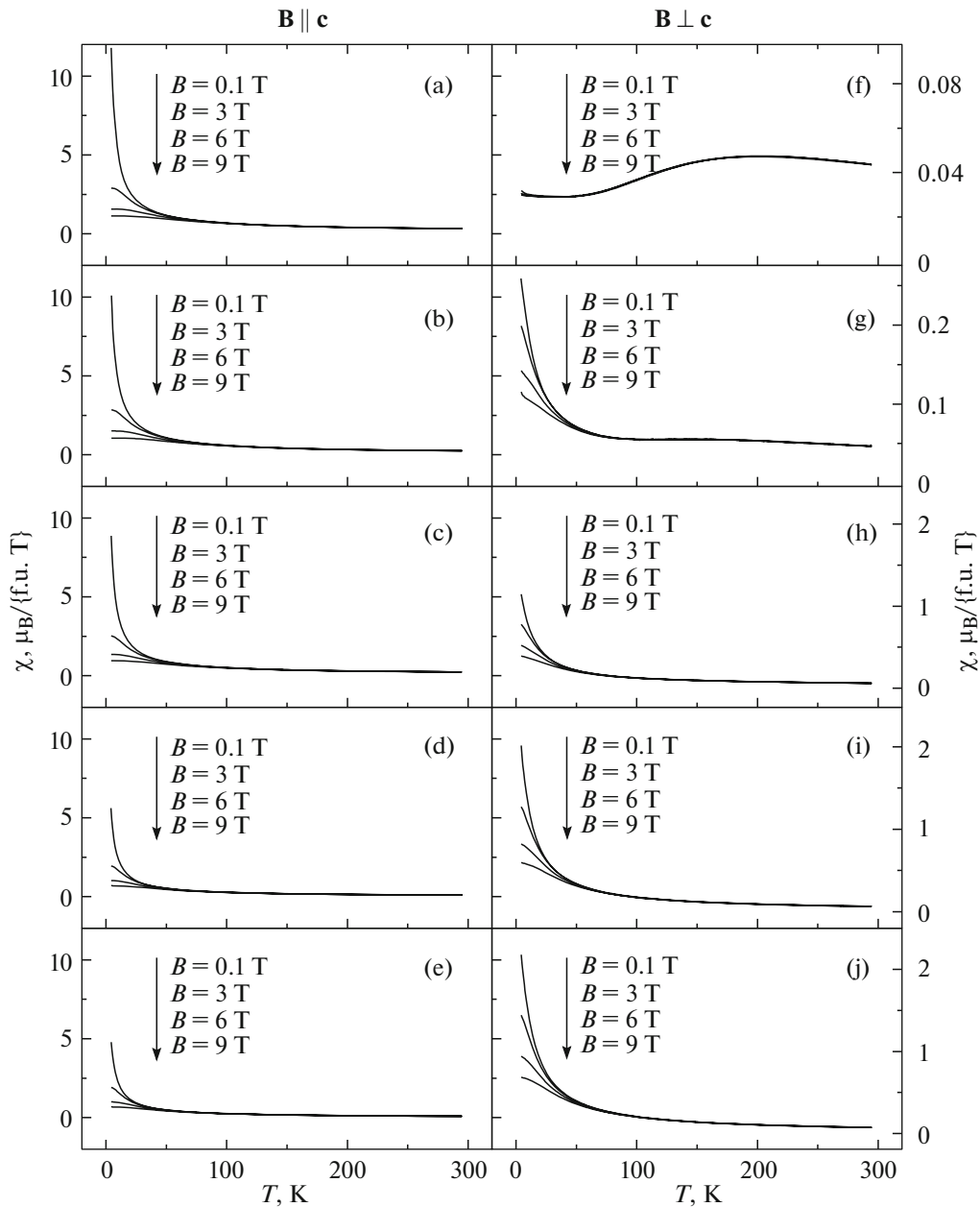


Fig. 1. Temperature dependences of $Tb_{1-x}Ho_xAl_3(BO_3)_4$ measured in various magnetic fields: $x =$ (a, f) 0, (b, g) 0.1, (c, h) 0.5, (d, i) 0.9, and (e, j) 1.

were grown on seeds on cooling at a rate of $1^\circ C/day$. The start temperature was $T = T_{sat} - 7^\circ C$. The crystals grown had sizes of $\sim 4-6$ mm. On completing the growth process, the crystals were cooled to room temperature at a rate that was not higher than $100^\circ C/h$.

The magnetic properties were studied in the temperature range of 4.2–300 K and in magnetic field to 9 T using a Quantum Design PPMS vibrating magnetometer.

3. RESULTS AND DISCUSSION

All aluminoborates with the huntite structure have a trigonal structure that belongs to space group $R32$. The magnetic properties of the grown single crystals $Tb_{1-x}Ho_xAl_3(BO_3)_4$ with $x = 0, 0.1, 0.5, 0.9, 1$ were studied in magnetic fields $B = 0.1, 3, 6,$ and 9 T at the orientations of the magnetic field along the third-order axis c and along axis a that was perpendicular to axis c .

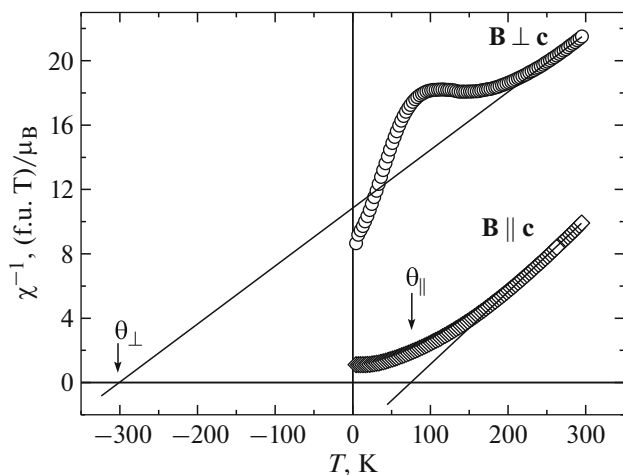


Fig. 2. Temperature dependence of the inverse magnetic susceptibility measured in magnetic field 9 T for the $\text{Tb}_{0.9}\text{Ho}_{0.1}\text{Al}_3(\text{BO}_3)_4$ composition.

Figure 1 shows the temperature dependences of the magnetic susceptibility of the single crystals expressed in the Bohr magnetons per formula unit. It is seen from Fig. 1 that dependences $\chi_{\parallel}(T)$ and $\chi_{\perp}(T)$ (exception for curves $\chi_{\perp}(T)$ for $\text{TbAl}_3(\text{BO}_3)_4$) have the same form for all compositions typical of paramagnets and are only different in magnitudes. At low temperatures, beginning from approximately 50 K, the temperature dependences of the susceptibility measured in various magnetic fields are different from each other. It is likely due to approaching the saturation point of paramagnetic materials.

Using the Curie–Weiss law, the paramagnetic Curie temperature θ and the effective magnetic moment of ion in the unit cell can be found from the high-temperature dependence of the magnetic susceptibility. Figure 2 shows such dependences for the $\text{Tb}_{0.9}\text{Ho}_{0.1}\text{Al}_3(\text{BO}_3)_4$ composition measured in magnetic field 9 T in various geometries of the experiment ($B \parallel c$ and $B \perp c$).

For $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$, Fig. 3 shows the dependences of the effective magnetic moments $\mu_{\text{eff}\parallel}$ and $\mu_{\text{eff}\perp}$ on parameter x measured in the magnetic field directions $B \parallel c$ and $B \perp c$, respectively. We observed a clear anisotropy of μ_{eff} . So, as x increases, $\mu_{\text{eff}\parallel}$ increased at $B \parallel c$, and $\mu_{\text{eff}\perp}$ decreased at $B \perp c$. In this case, dependence $\mu_{\text{eff}\perp}(x)$ was linear only at high $x \geq 0.5$. This is thought to be due to the following. As is seen from Figs. 1a and 1f, Tb^{3+} ion is an Ising ion as a quite good approximation. As the crystal was magnetized along the Ising c axis at low temperatures, the saturation was reached in relatively weak magnetic fields of 1–2 T. In the directions perpendicular to the c axis, the magnetic susceptibility was much lower and is nearly linearly dependent on the magnetic field and weakly dependent on temperature, which demon-

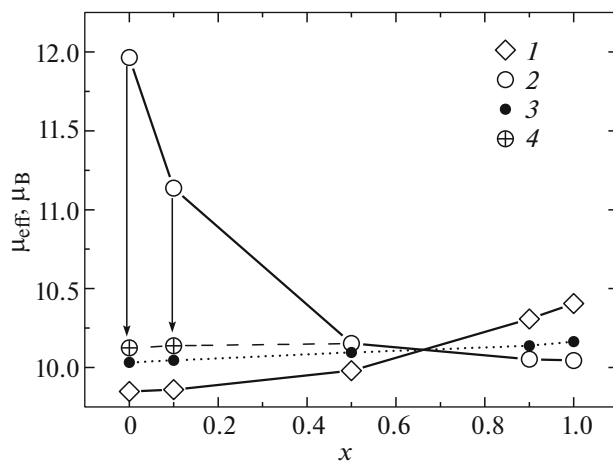


Fig. 3. Effective magnetic moments of the $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$ crystals obtained in magnetic fields (1) $B \parallel c$ and (2) $B \perp c$, (3) calculated values of $\mu_{\text{eff}\parallel}$ of $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$; (4) calculated values of $\mu_{\text{eff}\perp}$.

strates its Van Vleck origin; i.e., it was provided by adding excited states of Tb^{3+} ion to its ground state in magnetic field. Because of this, the temperature dependence of the magnetic susceptibility had a form noncharacteristic of the classical paramagnetic form (Fig. 1f), and the linear segment of temperature dependence of the inverse susceptibility $\chi^{-1}(T)$ begins at relatively high temperatures (~ 250 K). Because of this, our experiments contained a substantial error in determination of $\mu_{\text{eff}\perp}$ in the compositions with high content of Tb^{3+} ions. Thus, the values $\mu_{\text{eff}\perp} = 11.9\mu_B$ for $\text{TbAl}_3(\text{BO}_3)_4$ and $\mu_{\text{eff}\perp} = 11.1\mu_B$ for $\text{Tb}_{0.9}\text{Ho}_{0.1}\text{Al}_3(\text{BO}_3)_4$ (Fig. 2) need refinements.

Let us estimate the values of $\mu_{\text{eff}\perp}$ that must be for the compounds noted above. As is known, the effective magnetic moments of free Tb^{3+} and Ho^{3+} ions are $9.7\mu_B$ and $10.6\mu_B$, respectively. Then, for $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$, the value $\mu_{\text{eff}} = (1/3)\mu_{\text{eff}\parallel} + (2/3)\mu_{\text{eff}\perp}$ must increase linearly with x (3 in Fig. 3). In this case, $\mu_{\text{eff}\perp}$ of $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{Tb}_{0.9}\text{Ho}_{0.1}\text{Al}_3(\text{BO}_3)_4$ must be $10.12\mu_B$ and $10.14\mu_B$, respectively (4 in Fig. 3).

Figure 4 shows the temperature dependences of the difference between magnetic susceptibility χ_{cal} calculated and magnetic susceptibility χ_{exp} measured in a magnetic field of 9 T. The value χ_{cal} was calculated based on the fact that the contributions of Tb^{3+} and Ho^{3+} ions to the magnetic susceptibility are proportional to fractions from the susceptibilities of $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{HoAl}_3(\text{BO}_3)_4$, respectively: $\chi_{\text{cal}}(x) = (1-x)\chi_{\text{TbAl}_3(\text{BO}_3)_4} + x\chi_{\text{HoAl}_3(\text{BO}_3)_4}$. It is seen from Fig. 4 that χ_{exp} and χ_{cal} almost coincide at high temperatures. As temperature decreased, difference $\chi_{\text{cal}} - \chi_{\text{exp}}$ increased and significantly increased at temperatures

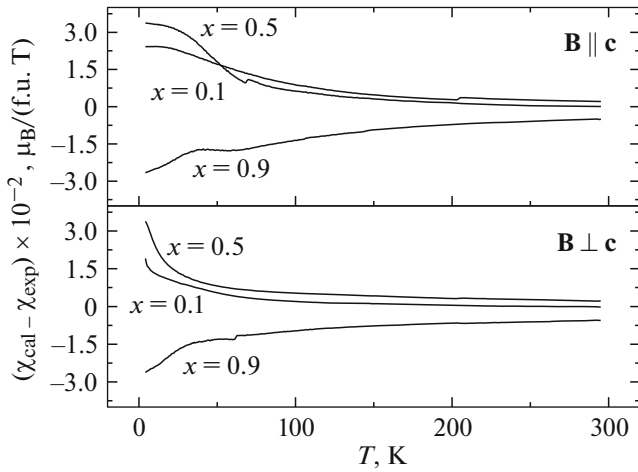


Fig. 4. Temperature dependence of difference $\chi_{\text{cal}} - \chi_{\text{exp}}$ for $\mathbf{B} \parallel \mathbf{c}$ and $\mathbf{B} \perp \mathbf{c}$ in magnetic field 9 T.

$T \approx 30\text{--}50$ K. In this case, $\chi_{\text{cal}} - \chi_{\text{exp}} > 0$ for the compositions with $x = 0.1$ and 0.5 and $\chi_{\text{cal}} - \chi_{\text{exp}} < 0$ for the composition with $x = 0.9$. The form of differences $\chi_{\text{cal}} - \chi_{\text{exp}}$ did not depend on the orientation and the value of magnetic field. Thus, paramagnetic chalcites of mixed compositions $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$ already cannot be considered as a simple superposition of paramagnets $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{HoAl}_3(\text{BO}_3)_4$. We could attempt to describe the character of the change in the magnetic properties of $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$ by the existence of exchange interaction between Tb^{3+} and Ho^{3+} ions, but this is unlikely because of a significant distance between these ions in the crystal lattice.

Most likely, such unusual behavior can be explained by a change in the single-ion anisotropy in $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$. As is known, the symmetric environment of a rare-earth ion in aluminoborates is described by a point group of symmetry D_3 . A rare-earth ion interacts with the crystal field and the external magnetic field

$$H = H_{\text{CF}} + g_j \mu_B \mathbf{J} \mathbf{B}, \quad (1)$$

where g_j is the Landé factor, \mathbf{J} is the angular momentum operator of a rare-earth ion, and H_{CF} is the Hamiltonian of the crystal field that can be written as

$$H_{\text{CF}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_{-3}^4 - C_3^4) + B_0^6 C_0^6 + B_3^6 (C_{-3}^6 - C_3^6) + B_6^6 (C_{-6}^6 - C_6^6), \quad (2)$$

where C_q^k are irreducible tensor operators and B_q^k are the parameters of the crystal field. For $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{HoAl}_3(\text{BO}_3)_4$, parameters B_q^k already were determined by optical spectroscopy [17, 18]: $B_0^2 = 581 \text{ cm}^{-1}$, $B_0^4 = -1254 \text{ cm}^{-1}$, $B_0^6 = -161 \text{ cm}^{-1}$, $B_3^4 = 815 \text{ cm}^{-1}$, $B_3^6 = 180 \text{ cm}^{-1}$, and $B_6^6 = 41 \text{ cm}^{-1}$ for $\text{TbAl}_3(\text{BO}_3)_4$,

and $B_0^2 = 491 \text{ cm}^{-1}$, $B_0^4 = -1150 \text{ cm}^{-1}$, $B_0^6 = 327 \text{ cm}^{-1}$, $B_3^4 = -797 \text{ cm}^{-1}$, $B_3^6 = -62 \text{ cm}^{-1}$, and $B_6^6 = -162 \text{ cm}^{-1}$ for $\text{HoAl}_3(\text{BO}_3)_4$. It is seen that the attendant parameters are significantly different not only in the value, but also sometimes in sign. The crystal field parameters

B_q^k are very sensitive to any substitutions; they are responsible for splitting of the main multiplet in the crystal field. As is known, the single-ion anisotropy is related to the fact that the magnetic ion energy is dependent on the orientation of the orbital moment with respect to the crystallographic axes, because of splitting the orbital levels by the crystal field and, therefore, is dependent on the spin orientation with respect to these axes due to the spin-orbital interaction. It is evident that the crystal field parameters for $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$ will change somehow with changing x ; in this case, is not clear that they will be changed linearly. It will be more correct to determine them experimentally and perform calculations in terms of any model.

4. CONCLUSIONS

The $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$ single crystals with $x = 0, 0.1, 0.5, 0.9, 1$ were grown by the solution-melt method on the basis of bismuth trimolybdate. Their magnetic properties were studied in wide ranges of temperatures and magnetic fields.

At low temperatures, beginning from approximately 50 K, the temperature dependences of the susceptibility measured at various magnetic fields are different from each other. It was assumed that this is due to approaching the saturation point of the paramagnetic crystal under study.

In terms of an approximation of the Curie-Weiss law, we found the effective magnetic moments $\mu_{\text{eff} \parallel}$ and $\mu_{\text{eff} \perp}$ of Tb^{3+} and Ho^{3+} ions in the unit cell of $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$.

The measured temperature dependences of the susceptibility of the compositions with $x = 0.1, 0.5$, and 0.9 are different from the temperature dependences calculated, assuming that the contributions of Tb^{3+} and Ho^{3+} ions to the magnetic susceptibility are proportional to fractions from the susceptibilities of $\text{TbAl}_3(\text{BO}_3)_4$ and $\text{HoAl}_3(\text{BO}_3)_4$, respectively. It was assumed that this behavior can be explained by a change in the single-ion anisotropy in $\text{Tb}_{1-x}\text{Ho}_x\text{Al}_3(\text{BO}_3)_4$.

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