

# Magnetic and Magnetoelectric Properties of Scandoborate $\text{NdSc}_3(\text{BO}_3)_4$

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**Abstract**—Trigonal neodymium scandoborate  $\text{NdSc}_3(\text{BO}_3)_4$  single crystals have been grown by the batch flux method using bismuth trimolybdate and their magnetic and magnetoelectric properties have been investigated in the temperature range of 4.2–300 K in magnetic fields of up to 9 T. Magnetically, the compound is a paramagnet and its properties are determined by the magnetic properties of the  $\text{Nd}^{3+}$  ion with allowance for the Van Vleck paramagnetic correction. The magnetoelectric polarization value has been found to be comparable with that of the previously investigated diluted neodymium aluminum borate  $\text{Nd}_{0.35}\text{Y}_{0.65}\text{Al}_3(\text{BO}_3)_4$ . The latter circumstance opens up another subclass of compounds that should exhibit the giant magnetoelectric effect.

**Keywords:** magnetoelectric effect, crystal growth, multiferroics

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## 1. INTRODUCTION

In the last decade, trigonal rare-earth oxyborates  $\text{RM}_3(\text{BO}_3)_4$  (R is a rare-earth ion and  $\text{M} = \text{Al}, \text{Sc}, \text{Fe}, \text{Ga}$ ) have been intensively studied due to the wide possibilities of combining elements R and M and, correspondingly, a great diversity in the physical properties. [1–8]. Oxyborates have a rhombohedral structure of the natural mineral huntite type, which is described by sp. gr.  $R\bar{3}2$  or  $P\bar{3}_121$ . The noncentrosymmetric structure makes these materials promising for optical applications due to their good luminescence and nonlinear optical properties. For ferrobates  $\text{RFe}_3(\text{BO}_3)_4$ , it was established that they belong to a new class of multiferroics with the coexisting magnetic, electrical, and elastic order parameters.

The interest in paramagnetic aluminoborates has increased since the discovery of the giant magnetoelectric effect in  $\text{TmAl}_3(\text{BO}_3)_4$  [9], which turned out to be comparable in value with the effects observed in isostructural ferrobates  $\text{RFe}_3(\text{BO}_3)_4$ . Later, the even greater magnetoelectric effect was discovered in  $\text{HoAl}_3(\text{BO}_3)_4$  [10], the value of which ( $\sim 5480 \mu\text{C}/\text{m}^2$ ) is several times higher than the known maximum values of the magnetoelectric polarization in ferrobates ( $\sim 500 \mu\text{C}/\text{m}^2$  in  $\text{SmFe}_3(\text{BO}_3)_4$  [5],  $\sim 300 \mu\text{C}/\text{m}^2$  in  $\text{NdFe}_3(\text{BO}_3)_4$  [3], and  $\sim 900 \mu\text{C}/\text{m}^2$  in

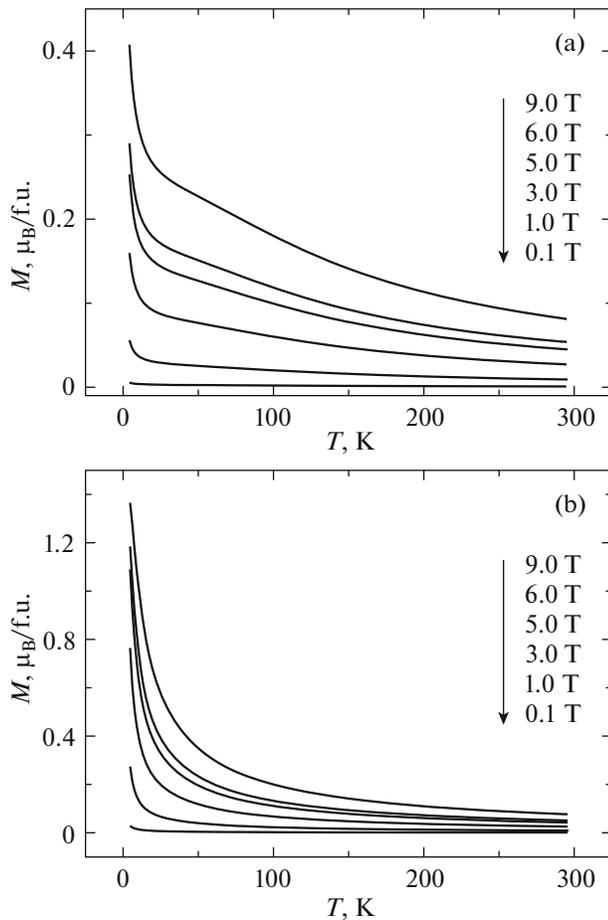
$\text{Ho}_{0.5}\text{Nd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  [3]). An increase in the magnetoelectric effect is observed also when  $\text{Fe}^{3+}$  ions in  $\text{HoFe}_3(\text{BO}_3)_4$  are replaced by  $\text{Ga}^{3+}$  ions [11].

Taking into account that, at the replacement of the magnetic (Fe) subsystem in  $\text{RM}_3(\text{BO}_3)_4$  by the nonmagnetic one (Al, Ga), the magnetoelectric effect attains giant values, it is interesting to explore other subclasses of the huntite-structure oxyborates with one magnetic subsystem, for example, the rare-earth scandoborates  $\text{RSc}_3(\text{BO}_3)_4$ . Scandoborate  $\text{NdSc}_3(\text{BO}_3)_4$  was chosen to be an object of study. The choice of this compound was additionally dictated by the fact that a stable  $\text{NdAl}_3(\text{BO}_3)_4$  trigonal phase does not exist and only the substituted aluminoborate  $\text{Nd}_{0.35}\text{Y}_{0.65}\text{Al}_3(\text{BO}_3)_4$  was previously examined [12].

In this work, we report on the results of magnetic and magnetoelectric investigations of scandoborate  $\text{NdSc}_3(\text{BO}_3)_4$ .

## 2. EXPERIMENTAL

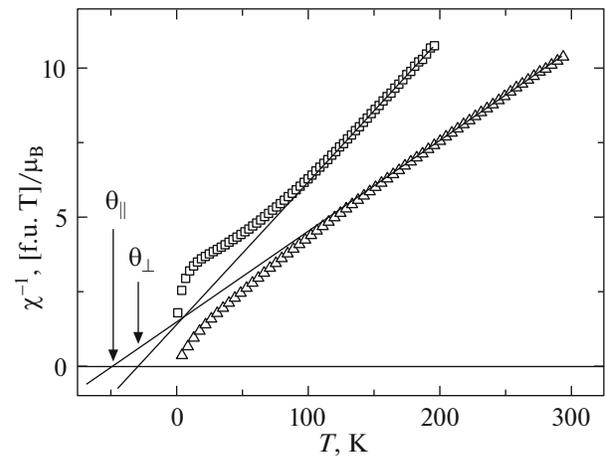
The  $\text{NdSc}_3(\text{BO}_3)_4$  single crystals were grown in mass on the basis of bismuth molybdate by the flux technique described in detail in [13]. It is convenient to present the flux system in the quasi-binary form 89 wt %  $[\text{Bi}_2\text{Mo}_3\text{O}_{12} + 3\text{Li}_2\text{O}_3 + 2\text{B}_2\text{O}_3 + 0.1\text{Nd}_2\text{O}_3]$  + 11 wt %  $\text{NdSc}_3(\text{BO}_3)_4$ .



**Fig. 1.** Temperature dependences of the magnetization for  $\text{NdSc}_3(\text{BO}_3)_4$  measured in different magnetic fields in the geometries (a)  $\mathbf{B} \parallel c$  and (b)  $\mathbf{B} \perp c$ .

The saturation temperature was refined accurate to  $\pm 2^\circ\text{C}$  using test crystals; for the investigated flux, it was found to be  $980^\circ\text{C}$ . The crystals were grown on seeds with a decrease in temperature at a rate of  $1^\circ\text{C}/\text{day}$ . The initial temperature was  $T = T_s - 7^\circ\text{C}$ . The grown crystals were about 4–6 mm in size. After the growth completion, the crystals were cooled down to room temperature at a rate of no more than  $100^\circ\text{C}/\text{h}$ .

The magnetic properties were investigated on a Quantum Design PPMS vibrating sample magnetometer at the Center for Collective Use, Krasnoyarsk Scientific Center of the Russian Academy of Sciences in the temperature range of 4.2–300 K and magnetic fields of up to 9 T and on an original vibrating sample magnetometer [14]. To measure the magnetoelectric polarization, electrodes made of epoxy resin with a conductive filler were formed on the face of a prepared plane-parallel plate sample (the face planes are perpendicular to the second-order ( $a$ ) axis). The charge induced on the sample by the magnetoelectric effect was measured with a Keithley 6517B electrometer. The



**Fig. 2.** Inverse temperature dependence of the magnetic susceptibility for  $\text{NdSc}_3(\text{BO}_3)_4$  measured in a magnetic field of 9 T in the geometries (a)  $\mathbf{B} \parallel c$  (triangles) and (b)  $\mathbf{B} \perp c$  (squares).

magnetic field was applied along the second-order crystallographic axis ( $a$  axis) and along the  $b$  axis perpendicular to the  $a$  axis and the third-order ( $c$ ) axis.

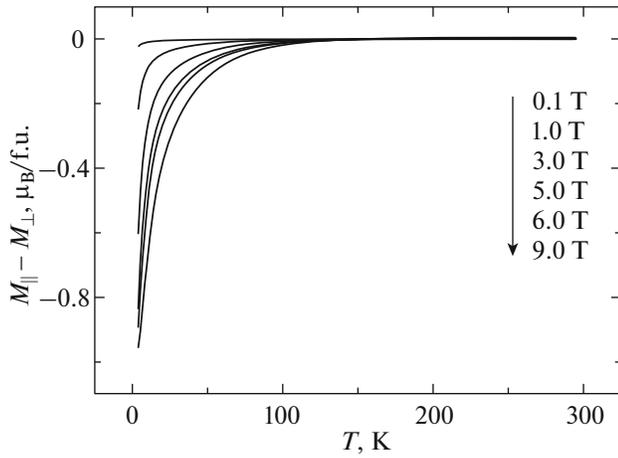
### 3. RESULTS AND DISCUSSION

As was shown previously, at high temperatures  $\text{NdSc}_3(\text{BO}_3)_4$  has a rhombohedral structure with sp. gr.  $R32$ . As the temperature decreases ( $T_s = 504$  K), the compound undergoes the structural transition  $R32 \rightarrow P3_121$  [12].

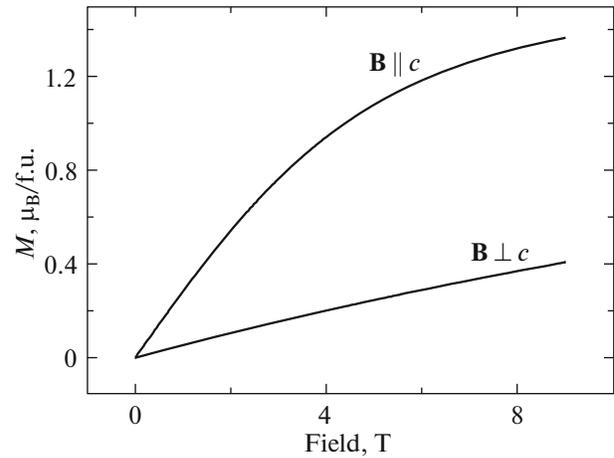
The magnetic properties were examined in magnetic fields of  $B = 0.1, 1, 3, 5, 6,$  and  $9$  T directed along the third-order  $c$  axis and the second-order  $a$  axis perpendicular to the  $c$  axis. Figure 1 shows temperature dependences of the magnetization in a magnetic field directed along and perpendicular to the third-order axis. One can see a trend to saturation upon magnetization along the  $c$  axis at low temperatures and, consequently, to the deviation from the Curie law (Fig. 2).

It can be seen for all the curves in Fig. 1 that the  $M(T)$  dependences have a similar form typical of a paramagnet and only have different values. With an increase in the field, the  $M_{\parallel}(T)$  and  $M_{\perp}(T)$  dependences increase at different rates, exhibiting a noticeable anisotropy (Fig. 3), which increases with the magnetic field.

In the directions  $\mathbf{B} \parallel c$ , the magnetization  $M_{\parallel}(T)$  is much lower than  $M_{\perp}(T)$ , depends almost linearly on the magnetic field (Fig. 4), and has a form atypical of classical paramagnets (Fig. 1a). This form of the  $M_{\parallel}(T)$  curve can be caused by admixing the excited states of the  $\text{Nd}^{3+}$  ion to the ground state. In other words, in determining the magnetic moment, one should take



**Fig. 3.** Temperature dependences  $M_{\parallel}-M_{\perp}$  for  $\text{NdSc}_3(\text{BO}_3)_4$  in different magnetic fields.



**Fig. 4.** Field dependences of the magnetization for  $\text{NdSc}_3(\text{BO}_3)_4$  at  $T = 4.2$  K in the geometry  $\mathbf{B} \parallel c$  and  $\mathbf{B} \perp c$ .

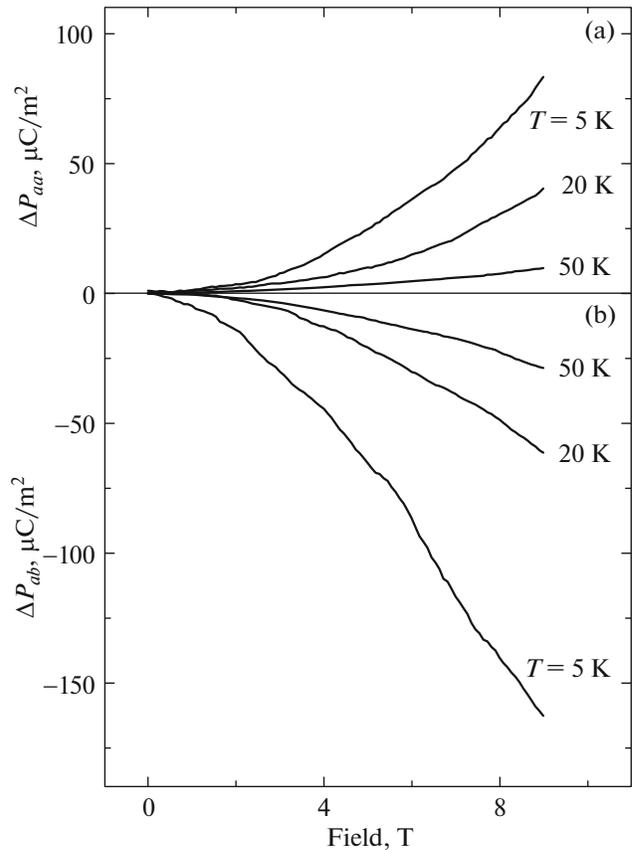
into account, along with the orientational paramagnetism, the Van Vleck correction.

Using the Curie–Weiss law, we can determine the paramagnetic Curie temperature  $\theta$  and the effective magnetic moment of the  $\text{Nd}^{3+}$  ion in the unit cell from the high-temperature dependence of the magnetic susceptibility. Figure 2 shows such a dependence obtained in a magnetic field of  $\mathbf{B} = 0.1$  T in different experimental geometries ( $\mathbf{B} \parallel c$  and  $\mathbf{B} \perp c$ ). The effective magnetic moment of the  $\text{NdSc}_3(\text{BO}_3)_4$  structural unit was found to be  $\mu_{\text{eff}} = 3.69\mu_B$ , which is close to the theoretical  $\mu_{\text{eff}}$  value taking into account the Van Vleck paramagnetism correction ( $\mu_{\text{eff}} = 3.68\mu_B$ ), while the theoretical magnetic moment of the  $\text{Nd}^{3+}$  ion determined as  $\mu = g\mu_B\sqrt{J(J+1)}$ , where  $g = 8/11$  is the  $g$  factor of the  $\text{Nd}^{3+}$  ion in free state, is  $\mu_{\text{Nd}} = 3.62\mu_B$ .

Figure 5 shows field dependences of the transverse ( $\Delta P_{ab}(B_b)$ ) and longitudinal ( $\Delta P_{aa}(B_a)$ ) magnetoelectric polarization of  $\text{NdSc}_3(\text{BO}_3)_4$  at different temperatures. As the field increases, the nonlinear growth of the  $\Delta P_{ab}$  and  $\Delta P_{aa}$  curves is observed. Such a course of the magnetoelectric polarization curves is typical of paramagnetic huntites [9–11].

A significant anisotropy of the magnetoelectric polarization at different magnetic field directions was found. It can be seen in Fig. 5 that the transverse polarization attains  $\Delta P_{ab}(B_b) \sim -163 \mu\text{C}/\text{m}^2$  and the longitudinal polarization,  $\Delta P_{aa}(B_a) \sim 83 \mu\text{C}/\text{m}^2$  at a temperature of  $T = 5$  K in a field of 9 T. These values exceed the values for the previously investigated neodymium aluminoborate  $\text{Nd}_{0.35}\text{Y}_{0.65}\text{Al}_3(\text{BO}_3)_4$ , for which we have  $\Delta P_{ab}(B_b) \sim -68 \mu\text{C}/\text{m}^2$  and  $\Delta P_{aa}(B_a) \sim 69 \mu\text{C}/\text{m}^2$  at  $T = 5$  K and  $H = 9$  T. However, if we take into account that the concentration of  $\text{Nd}^{3+}$  ions in the aluminum borate is lower than in neodymium scandoborate by a factor of  $1/0.35 \approx 3$ , then it can be

assumed that the growth of the effect upon replacement of Al (in  $\text{Nd}_{0.35}\text{Y}_{0.65}\text{Al}_3(\text{BO}_3)_4$ ) by Sc (in  $\text{NdSc}_3(\text{BO}_3)_4$ ) is explained by an increase in the con-



**Fig. 5.** Field dependences of the longitudinal magnetoelectric polarization  $\Delta P_a$  at different temperatures in the geometries (a)  $\mathbf{B} \parallel a$  and (b)  $\mathbf{B} \parallel b$ .

centration of magnetically active  $\text{Nd}^{3+}$  ions. On the other hand, as was previously shown, the magnetoelectric effect can be higher than expected due to the change in the energy structure of the rare-earth ion under local distortions [15]. The local distortions in  $\text{Nd}_{0.35}\text{Y}_{0.65}\text{Al}_3(\text{BO}_3)_4$  are obviously caused by the different  $\text{Al}^{3+}$  and  $\text{Y}^{3+}$  ionic radii and nonuniform distribution of the ions over the crystal matrix. Thus, now we cannot say which of the  $\text{RAl}_3(\text{BO}_3)_4$  and  $\text{RSc}_3(\text{BO}_3)_4$  matrices will give the greatest effect. This requires further investigations. We only can unambiguously state that  $\text{Sc}^{3+}$  ions, along with  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  ones, induce the giant magnetoelectric effect in the rare-earth oxyborates  $\text{RM}_3(\text{BO}_3)_4$  (R is a rare-earth ion and  $\text{M} = \text{Al}, \text{Sc}, \text{Ga}$ ) with a huntite structure.

#### 4. CONCLUSIONS

Scandoborate  $\text{NdSc}_3(\text{BO}_3)_4$  was grown by the batch flux method using bismuth trimolybdate. Its magnetic and magnetoelectric properties were first investigated in the temperature range of 4.2–300 K and magnetic fields of up to 9 T.

Magnetically,  $\text{NdSc}_3(\text{BO}_3)_4$  is a paramagnet, the properties of which are entirely determined by the magnetic behavior of the  $\text{Nd}^{3+}$  ion. The paramagnetic Curie temperature ( $\theta_{\perp} = -28$  K and  $\theta_{\parallel} = 48$  K) and the effective moment  $\mu_{\text{eff}} = 3.69\mu_{\text{B}}$  per formula unit were determined. It was shown that  $\mu_{\text{eff}}$  is close to its theoretical value, taking into account the Van Vleck paramagnetism contribution ( $\mu_{\text{eff}} = 3.68\mu_{\text{B}}$ ).

A significant anisotropy of the magnetoelectric polarization in different magnetic field directions was observed:  $\Delta P_{ab}(B_b) \sim -163 \mu\text{C}/\text{m}^2$  and  $\Delta P_{aa}(B_a) \sim 83 \mu\text{C}/\text{m}^2$  at a temperature of  $T = 5$  K in a field of 9 T. The effect in  $\text{NdSc}_3(\text{BO}_3)_4$  is weaker than in the previously investigated diluted neodymium aluminoborate  $\text{Nd}_{0.35}\text{Y}_{0.65}\text{Al}_3(\text{BO}_3)_4$ ; however, this can be caused by a change in the energy structure of the rare-earth  $\text{Nd}^{3+}$  ion in  $\text{Nd}_{0.35}\text{Y}_{0.65}\text{Al}_3(\text{BO}_3)_4$  under local distortions due to the different ionic radii of  $\text{Al}^{3+}$  and  $\text{Y}^{3+}$  and the non-uniform distribution of the ions over the crystal matrix.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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