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**ORDER, DISORDER, AND PHASE TRANSITION  
IN CONDENSED SYSTEM**

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# Peculiarities in the Magnetic, Magnetoelectric, and Magnetoelastic Properties of $\text{SmFe}_3(\text{BO}_3)_4$ Multiferroic

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**Abstract**—Results of a complex investigation of the magnetic, magnetoelectric, and magnetoelastic properties of a  $\text{SmFe}_3(\text{BO}_3)_4$  single crystal are presented. Samarium iron borate is similar to another easy-plane iron borate,  $\text{NdFe}_3(\text{BO}_3)_4$ , in that it possesses a large value of the magnetic-field-induced polarization (about  $500 \mu\text{C}/\text{m}^2$ ), the sign of which changes when the field direction is changed between axes  $a$  and  $b$  of the crystal. However, the temperature dependence of the magnetic susceptibility and the field dependence of polarization and magnetostriction of the two compounds are significantly different, which is explained by the weak effect of external magnetic field on the ground-state multiplet of samarium ion, which is characterized by an extremely small value of its  $g$ -factor.

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## 1. INTRODUCTION

Rare-earth iron borates with the general formula  $\text{RFe}_3(\text{BO}_3)_4$  (where R is a rare earth element) were earlier mostly treated as magnetic and optical materials [1, 2], but in recent years they have also received additional attention due to their magnetoelectric properties [3–9]. Below the Néel temperature ( $T_N = 30\text{--}40$  K), these iron borates exhibit an antiferromagnetic (AFM) ordering of  $\text{Fe}^{3+}$  ions. Depending on the particular rare earth ion, a crystal possesses either an easy-axis AFM structure, with iron spins aligned in the trigonal axis, or an easy-plane structure with these spins ordered in the  $ab$  plane (perpendicular to the  $c$  axis) of the crystal.

The easy-axis iron borates exhibit a magnetic-field-induced polarization that does not exceed tens of  $\mu\text{C}/\text{m}^2$  [6–8], whereas that in the easy-plane neodymium iron borate reaches several hundreds and even thousands of  $\mu\text{C}/\text{m}^2$  [4], thus giving this compound a special position among rare-earth iron borates.

In this context, it is of interest to study the properties of a rare-earth iron borate containing samarium ions, which are much like neodymium ions in that both are Kramers ions, they exhibit easy-plane-type anisotropy, and have close ion radii. A comparative analysis of the magnetic, magnetoelectric, and magnetoelastic properties of  $\text{SmFe}_3(\text{BO}_3)_4$  and other rare-earth iron borates can reveal factors that account for the magnitude of magnetic-field-induced polarization in this class of multiferroics.

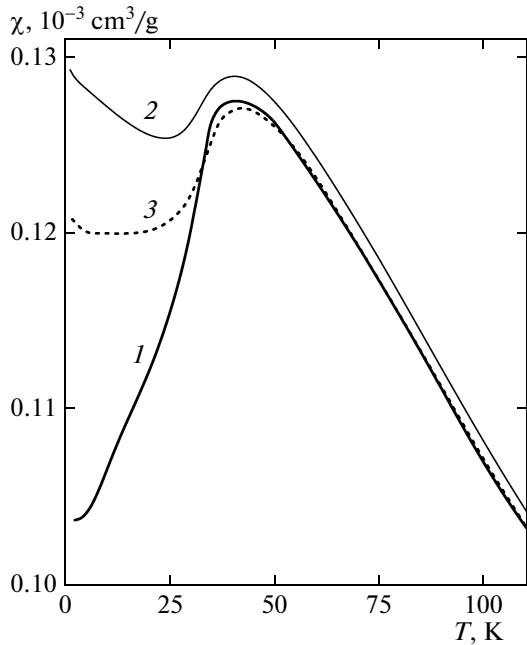
## 2. EXPERIMENTAL METHODS

Single crystals of  $\text{SmFe}_3(\text{BO}_3)_4$  in the form of cubes with an edge length of 2 mm were obtained by spontaneous crystallization from a solid solution melt. The magnetic properties of samples were studied in constant magnetic fields up to 50 kOe using a SQUID magnetometer (MPMC-5, Quantum Design). The magnetoelectric and magnetoelastic properties were measured in pulsed magnetic fields with amplitudes up to 250 kOe. The electric polarization was measured using electrodes of an epoxy resin with conductive filler, which were applied onto the crystal faces perpendicular to the magnetic field direction. Magnetostriction was measured using a piezoelectric sensor that represented a piezoelectric quartz plate glued onto the sample, which responded to the strain applied in only one direction. For magnetic field pulse durations of about 10 ms, the time of the charge leak-off was two to three orders of magnitude longer than the duration of measurements, which ensured reliability of the experimental results.

## 3. RESULTS AND DISCUSSION

### 3.1. Magnetic Properties

Figure 1 shows the temperature dependence of the magnetic susceptibility  $\chi$  of a  $\text{SmFe}_3(\text{BO}_3)_4$  single crystal. In the paramagnetic region, the susceptibility is nearly isotropic and obeys the Curie–Weiss law. At  $T < T_N \approx 40$  K,  $\chi$  becomes anisotropic: it drops sharply

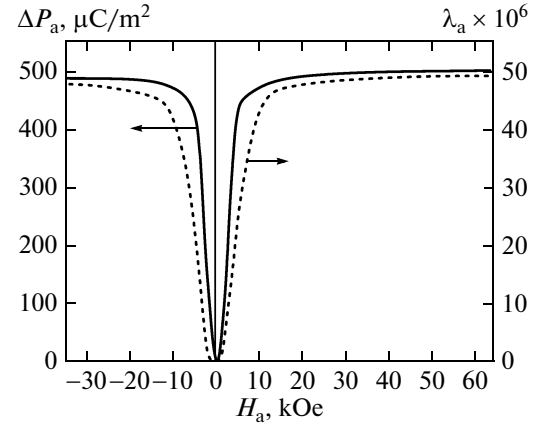


**Fig. 1.** Temperature dependence of the magnetic susceptibility  $\chi = M/H$  of a  $\text{SmFe}_3(\text{BO}_3)_4$  single crystal, determined by measuring the magnetization  $M$  in a magnetic field of  $H = 1$  kOe applied (1) perpendicular and (2) parallel to the  $c$  axis. Curve 3 presents the results of measurements at  $H = 10$  kOe, for which iron spins exhibit reorientation in the basal plane that is perpendicular to the field.

in the basal plane, but varies only slightly in the direction of the  $c$  axis, where it retains approximately the same value as that at the Néel point. This behavior indicates that  $\text{Fe}^{3+}$  ion spins are ordered in the basal plane. The final value of susceptibility in this plane is determined by the existing distribution of easy axes, which is controlled by the natural hexagonal anisotropy and/or induced magnetoelastic anisotropy. Application of magnetic field with  $H \approx 10$  kOe in the plane leads to rotation of ion spins and aligns them perpendicular to the applied field, imparting the crystal with a constant transverse susceptibility of  $\chi_{\perp}^{\text{Fe}} \approx 0.12 \times 10^{-3} \text{ cm}^3/\text{g}$ .

The observed temperature dependences of the magnetic susceptibility in  $\text{SmFe}_3(\text{BO}_3)_4$  differs significantly from analogous curves for another easy-plane iron borate,  $\text{NdFe}_3(\text{BO}_3)_4$ , and most likely resemble the behavior of  $\chi(T)$  in yttrium iron borate,  $\text{YFe}_3(\text{BO}_3)_4$ , where the contribution from the rare earth ion is absent [10]. This behavior is indicative of an anomalously small magnetic contribution of  $\text{Sm}^{3+}$  ions, which is related to features of their ground-state multiplet ( ${}^6H_{5/2}$ ), which is characterized by a small value of the  $g$ -factor of  $\text{R}^{3+}$  ions ( $g_{\text{R}} = 2/7$ ). This accounts for the very weak Zeeman effect of the magnetic field on the ground-state multiplet described by the Hamiltonian:

$$\hat{H} = \mu_{\text{B}} g_{\text{R}} \mathbf{J} \cdot \mathbf{H},$$



**Fig. 2.** Effect of the magnetic field applied along the  $a$  axis on the (solid curve) magnetic-field-induced polarization  $\Delta P_a$  and (dashed curve) magnetostriction  $\lambda_a = u_{xx}$  of a  $\text{SmFe}_3(\text{BO}_3)_4$  single crystal.

where  $\mu_{\text{B}}$  is the Bohr magneton,  $\mathbf{J}$  is the total moment of the rare earth ion, and  $\mathbf{H}$  is the external magnetic field. At the same time, this feature of the ground-state multiplet of  $\text{Sm}^{3+}$  ions does not influence the isotropic R–Fe exchange interaction:

$$\hat{H}_{\text{R-Fe}} = I(\mathbf{S}_{\text{R}} \cdot \mathbf{S}_{\text{Fe}}),$$

where  $I$  is the exchange integral and  $\mathbf{S}_{\text{R}}$  and  $\mathbf{S}_{\text{Fe}}$  are the spins of the rare earth and iron ions, respectively.

### 3.2. Magnetolectric and Magnetoelastic Properties

Figure 2 shows the dependences of the electric polarization  $\Delta P_a$  and magnetostriction  $\lambda_a$  of a single crystal of  $\text{SmFe}_3(\text{BO}_3)_4$  on the magnetic field at a temperature of 4.2 K. In relatively small fields (below 10 kOe), both these quantities exhibit a sharp (jump-like) increase, which is related to the establishment of a homogeneous AFM order in the entire crystal volume. Analogous anomalies have been observed in yttrium iron borate,  $\text{YFe}_3(\text{BO}_3)_4$ , but the value of the magnetic-field-induced polarization in samarium iron borate is much greater, close to that in neodymium iron borate (Fig. 3).

As was demonstrated earlier [4], the longitudinal polarization and magnetostriction consist of both contributions due to the AFM order parameter  $\mathbf{l}$  and magnetic moments  $m_i$  of rare earth ions magnetized in the  $f$ – $d$  exchange field, which form two paramagnetic sublattices:

$$P_x = c_1 l_y l_x + c_2 (l_x^2 - l_y^2) + \frac{1}{2} \sum_{i=1}^2 [c_3 (m_{ix}^2 - m_{iy}^2) + c_5 m_{iz} m_{iy}], \quad (1)$$

$$u_{xx} - u_{yy} = b_1 l_y l_z + b_2 (l_x^2 - l_y^2) + \frac{1}{2} \sum_{i=1}^2 [b_3 (m_{ix}^2 - m_{iy}^2) + b_4 m_{iz} m_{iy}]. \quad (2)$$

Here, the sums are taken over two rare-earth sublattices ( $i = 1, 2$ ); subscripts  $x$ ,  $y$ , and  $z$  refer to the crystallographic directions  $a$ ,  $b$ , and  $c$ , respectively. Coefficients  $b_i$  and  $c_i$  in Eqs. (1) and (2) are the same for both sublattices, which is explained by the fact that all rare earth ions occupy the same crystallographic sites and only the exchange fields that act upon these ions are different.

Formulas (1) and (2) suggest that the transition to a homogeneous AFM order in easy-plane iron berates must be accompanied by jumps in polarization and magnetostriction, which accounts for the qualitative similarity of the field dependences of polarization and magnetostriction for  $\text{SmFe}_3(\text{BO}_3)_4$  to analogous characteristics of non-lanthanide iron borate  $\text{YFe}_3(\text{BO}_3)_4$  [for which the terms related to  $m_i$  components in formula (1) vanish] and for the quantitative coincidence of the polarization values in  $\text{SmFe}_3(\text{BO}_3)_4$  and  $\text{NdFe}_3(\text{BO}_3)_4$ .

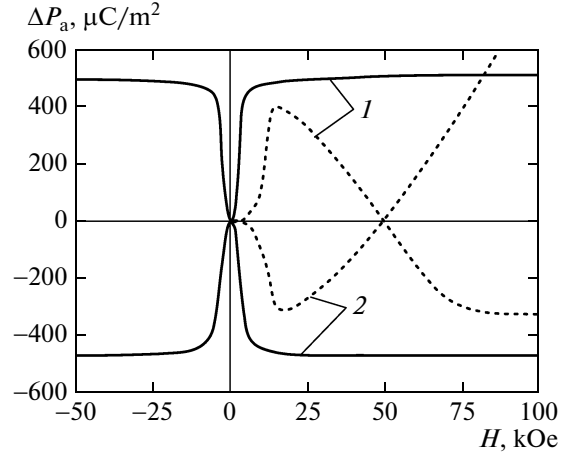
The initial inhomogeneity can be related to the presence of both the AFM domains and structures spatially modulated along the  $c$  axis, the existence of which has been established in gadolinium iron borate [11] and neodymium iron borate [12].

A characteristic feature inherent to both samarium iron borate and neodymium iron borate is the difference in signs of the longitudinal  $P_a(H_a)$  and transverse  $P_a(H_b)$  electric polarizations (see Fig. 3). This is a direct result of the symmetry treatment, since expression (1) contains terms proportional to  $l_x^2 - l_y^2$  and  $m_{ix}^2 - m_{iy}^2$ , which change signs when the magnetic field direction is rotated by  $90^\circ$ .

### 3.3. Behavior of Magnetoelectric Curves in High Fields

As can be seen from Fig. 3, the magnetoelectric properties of samarium and neodymium iron berates, rather similar in small magnetic fields, exhibit significant differences in stronger fields. In  $\text{SmFe}_3(\text{BO}_3)_4$ , the magnetic-field-induced polarization saturates at about 20 kOe and then remains unchanged up to very high fields, whereas in  $\text{NdFe}_3(\text{BO}_3)_4$ , the polarization changes sign in a field of about 50 kOe. Analogous behavior was observed for the magnetostriction of neodymium iron borate [4].

As was demonstrated earlier [4], these phenomena can be explained using a model according to which rare earth ions occur in a field that comprises the sum of external magnetic field  $H$  and exchange interaction field  $H_{\text{Fe-R}}$ . The latter field is generated by the iron subsystem and acts in the transverse direction. When the external field equilibrates the magnetizing action



**Fig. 3.** Effect of the (1) longitudinal magnetic field applied along axis  $a$  and (2) transverse magnetic field applied along axis  $b$  on the magnetic-field-induced polarization  $\Delta P_a$  in iron berates of (solid curves)  $\text{SmFe}_3(\text{BO}_3)_4$  and (dashed curves)  $\text{NdFe}_3(\text{BO}_3)_4$ .

of the exchange field, the terms proportional to  $m_{ix}^2 - m_{iy}^2$  change signs, and this results in the change of signs of both the magnetoelectric polarization (1) and magnetostriction (2).

The critical value of the external magnetic field, which can change (switch) the signs of the magnetoelectric polarization and magnetostriction, is determined by the relative magnitude of the Zeeman contribution to the ion energy as compared to the Fe–R exchange interaction. As was pointed out above, this exchange is related to the interaction of spin moments of the rare earth ( $\mathbf{S}_R$ ) and iron ( $\mathbf{S}_{\text{Fe}}$ ) ions:  $H_{\text{Fe-R}} = I \mathbf{S}_R \cdot \mathbf{S}_{\text{Fe}}$ , where  $I$  is the exchange integral that depends on the bond lengths and angles in the  $\text{R}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$  molecular configuration. At the same time, the external magnetic field acts upon the total moment  $\mathbf{J}_R$ , the corresponding contribution to the energy is given by the product  $\mu_{\text{B}} g_R \mathbf{J}_R \cdot \mathbf{H}$ . The smaller the  $g$ -factor, the greater the external field must be in order to produce an effect comparable to that of the exchange field.

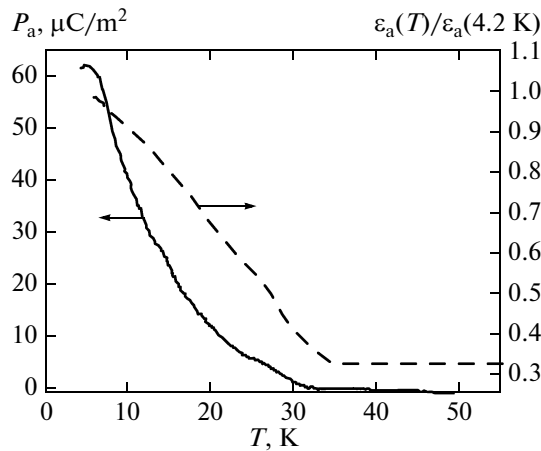
Using well-known relations between the operators of orbital ( $\mathbf{L}$ ), spin ( $\mathbf{S}_R$ ), and total moment ( $\mathbf{J}$ ) and the magnetic moment ( $\mathbf{M}_R$ ) of rare earth ions,

$$\mathbf{J} = \mathbf{L} + \mathbf{S}_R, \quad \mathbf{L} + 2\mathbf{S}_R = g_R \mathbf{J}, \quad \mathbf{M}_R = J g_R \mu_B,$$

we obtain the following expression for the critical value of the external field:

$$H_c = -\frac{I S_R S_{\text{Fe}}}{M} = -\frac{I (g_R - 1)}{\mu_B g_R} S_{\text{Fe}}. \quad (3)$$

Assuming, to a first approximation, that the exchange integrals  $I$  for two different rare earth ions are close (which is valid at least for ions with close radii) and using the experimentally measured (Fig. 3) values of the switching field for neodymium iron borate



**Fig. 4.** Temperature dependence of the (solid curve) spontaneous polarization  $P_a$  and (dashed curve) dielectric permittivity  $\epsilon_a$  of a  $\text{SmFe}_3(\text{BO}_3)_4$  single crystal.

( $H_{\text{Fe-R}}^{\text{Nd}} \approx 50$  kOe), we obtain from formula (3) the following values of the critical (switching) field in samarium iron borate:

$$H_c^{\text{Sm}} = H_{\text{Fe-R}}^{\text{Nd}} \frac{g_{\text{Sm}} - 1}{g_{\text{Sm}}} \frac{g_{\text{Nd}}}{g_{\text{Nd}} - 1} \approx 300 \text{ kOe}.$$

This estimate explains the fact that no change in the signs of magnetoelectric polarization and magnetostriction are observed in samarium iron borate, in contrast to that observed for neodymium iron borate at 50 kOe. Indeed, the critical (switching) field for samarium iron borate (about 300 kOe) is outside the range of the field accessible in the experiment. The weak effect of the external magnetic field on the ground-state multiplet of  $\text{Sm}^{3+}$  ions agrees well with the measurement results of the magnetic properties of samarium iron borate (Fig. 1).

### 3.4. Spontaneous Electric Polarization

Below the Néel temperature, the magnetic order induces a magnetoelectric polarization that is manifested, as noted above, in fields above 10 kOe, where homogeneous AFM ordering takes place (Fig. 2). However, even in the absence of external magnetic field, samarium iron borate can acquire a nonzero polarization (Fig. 4) under the action of factors that reduce the crystal symmetry. One of these factors is uniaxial anisotropy induced by mechanical stresses via magnetoelastic interactions.

It is possible that such symmetry violation is related to significant spontaneous polarization of samarium iron borate (Fig. 4, solid curve) amounting to more than 10% of the saturation level in the magnetoelectric polarization (Fig. 2).

The establishment of a magnetic order is accompanied by anomalies on the temperature dependence of

the dielectric permittivity  $\epsilon_a$  (Fig. 4, dashed curve) near the Néel temperature, the behavior of which differs from that according to the Curie–Weiss law. This observation is indicative of the extrinsic nature of the observed electric polarization. As is known, multiferroics with improper ferroelectric polarization induced by the magnetic ordering exhibit most pronounced magnetoelectric properties [13].

## 4. CONCLUSIONS

The presence of spontaneous polarization and mutually correlated magnetoelectric and magnetoelastic properties allows us to classify  $\text{SmFe}_3(\text{BO}_3)_4$  as multiferroics. In the series of rare-earth iron borates,  $\text{SmFe}_3(\text{BO}_3)_4$  is distinguished, like  $\text{NdFe}_3(\text{BO}_3)_4$ , by its large value of magnetic-field-induced polarization (about  $500 \mu\text{C}/\text{m}^2$ ), which is related to the easy-plane character of anisotropy in both these compounds, which allows the contribution of the magnetic subsystem of rare earth ions to the magnetoelectric polarization.

Differences observed in the field dependences of the polarization in  $\text{SmFe}_3(\text{BO}_3)_4$  and  $\text{NdFe}_3(\text{BO}_3)_4$  can be explained by the large (about 300 kOe) value of the critical field at which the polarization and magnetostriction signs are switched in samarium iron borate. This is related to an extremely small value of the  $g$ -factor of samarium ion in the ground state, which is confirmed by the results of measurements of the magnetic properties of samarium iron borate. At the same time, the isotropic exchange interaction between rare earth and iron ions is not affected. This fact as well as easy-plane anisotropy of samarium iron borate agrees with recent spectroscopic results [14].

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