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LOW-TEMPERATURE SOLID-STATE PHYSICS

Magnetoelectric Interactions in Rare-Earth Ferroborates

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Abstract—Magnetic-field-induced phase transitions in single crystals of the rare-earth ferroborates $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$ have been studied by measuring magnetoelectric dependences and torque curves. These phase transitions can serve as one of the possible mechanisms for magnetic control of electric polarization. Magnetic phase transitions in $GdFe_3(BO_3)_4$ are analyzed theoretically.

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Interest in rare-earth ferroborates has quickened in the past few years, since they were found to belong to a new family of magnetoelectric materials [1, 2]. The gadolinium ferroborate $GdFe_3(BO_3)_4$ has received the most study among them: its properties were comprehensively studied by magnetic, resonance, optical, thermodynamic, magnetoelectric, and magnetoelastic methods [1, 3–12]. At temperatures below $T_N = 38$ K, this material becomes antiferromagnetic, and its spins are oriented in the basal plane ($AF_\perp$ phase) [3, 4, 7, 11]. At $T = T_{SR} = 10$ K, a spontaneous transition occurs, and the spins of Fe^{3+} are reoriented toward the c axis of the crystal ($AF_\parallel$ phase) [3, 4, 7, 11]. The formation of the magnetic properties of rare-earth ferroborates at low temperatures depends substantially on the interaction between rare-earth and iron ions. Since the free Gd^{3+} and Fe^{3+} ions are in the S state ($L = 0$), the Gd–Fe exchange in this compound should be isotropic. However, the presence of the spontaneous spin-reorientation transition at $T_{SR} \approx 10$ K in $GdFe_3(BO_3)_4$ indicates an anisotropic character of the *f–d* exchange, as in $GdFeO_3$ and $GdCrO_3$ [13]. This means that the Gd–Fe exchange theory should take into account not only the ground S state of the Gd^{3+} and Fe^{3+} ions but also their excited states with a nonzero orbital moment. Therefore, it is interesting to compare the magnetic and magnetoelectric properties of $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$, in which the Nd^{3+} ions are Kramers ions with ground state $^4I_{9/2}$.

The authors of [1, 2] were the first to show that the magnetoelectric interaction in these compounds manifests itself as anomalies in the magnetic-field dependence of electric polarization and that these anomalies accompany changes in the antiferromagnetic order of the iron sublattice. Using these anomalies, we detected an unusual $AF_\parallel \longrightarrow AF_\perp$ transition in $GdFe_3(BO_3)_4$ induced by a magnetic field $\mathbf{H} \perp \mathbf{c}$ at $T < T_{SR}$ (Fig. 1a), apart from spin reorientation at T_{SR} and a spin-flop transition at $\mathbf{H} \parallel \mathbf{c}$.

Down to the lowest temperatures (about 1 K), we may neglect the Gd^{3+}–Gd^{3+} interaction, since these ions can be considered as independent paramagnetic ions subjected to the action of an effective field $\mathbf{H}_{\text{eff}}$, which includes the *f–d* exchange field $\mathbf{H}_{\text{exch}}$ (exchange interaction between the iron and rare-earth subsystems), a correction $\delta\mathbf{H}$ related to the *f–d* exchange anisotropy, and an applied field $\mathbf{H}$:

$$\mathbf{H}^i_{\text{eff}} = \mathbf{H}^i_{\text{exch}} + \delta\mathbf{H}^i + \mathbf{H}. \tag{1}$$

Since the iron subsystem is antiferromagnetically ordered, rare-earth ions in the exchange fields of two antiferromagnetic iron subsystems are also divided into two paramagnetic subsystems [2], and superscript $i = 1, 2$ demonstrates to which of the subsystems field (1) belongs.

The rare-earth subsystem in field (1) gives the following contribution to the thermodynamic potential of the gadolinium subsystem:

$$\begin{aligned} F_{\text{Gd}} &= -\frac{1}{2}\sum_{i=1}^{2}\int_0^{H^i_{\text{eff}}} M_{\text{Gd}}(H_{\text{eff}})dH_{\text{eff}} \\ &= -\frac{kT}{2}\sum_{i=1}^{2}\int_0^{x_i} B_J(x)dx, \end{aligned} \tag{2}$$

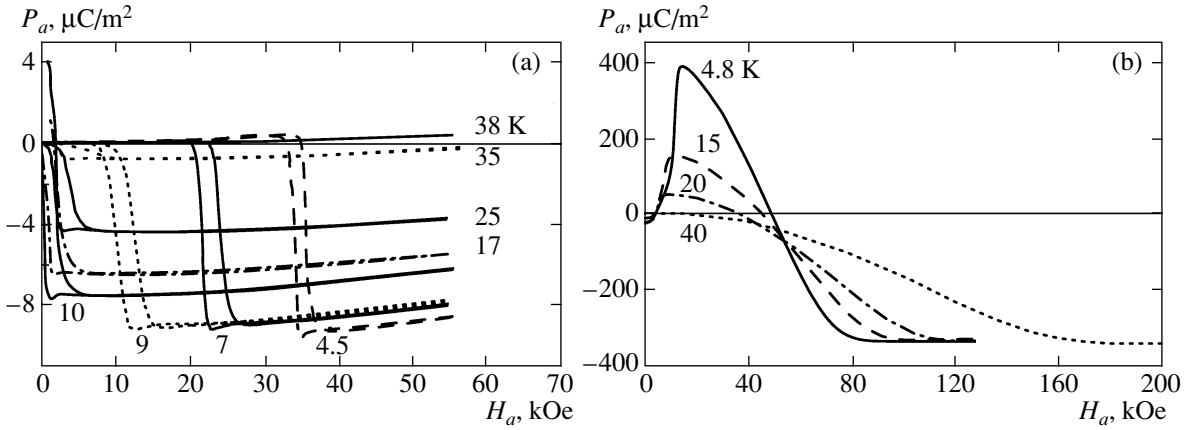

Fig. 1. Dependences of the longitudinal polarization on the magnetic field H_a directed along the a axis for (a) $GdFe_3(BO_3)_4$ and (b) $NdFe_3(BO_3)_4$ recorded at various temperatures.

where M_{Gd} is the magnetic moment of gadolinium; summation is taken over two paramagnetic subsystems $i = 1, 2$; and $B_J(x)$ is the Brillouin function, $x = g\mu_B JH_{eff}/kT$, where g is the Landé factor, μ_B is the Bohr magneton, $J = 7/2$ is the quantum number of the total angular momentum of the gadolinium ion.

During spontaneous spin reorientation ($T_{SR} = 10$ K), the uniaxial anisotropy constant K changes its sign ($F_{anys} = K\cos^2\theta$, where θ is the angle between the direction of the spins of iron atoms and the c axis). In this case, the constant K consists of the contributions of the iron (K^{Fe}) and rare-earth (K^{Gd}) subsystems. Thus, for spin reorientation, we obtain

$$K^{Fe} + K^{Gd}(T_{SR}) = 0. \quad (3)$$

We naturally assume here that the temperature dependence is substantial only for the rare-earth sublattice (which is responsible for the transition at T_{SR}) and that the anisotropy parameters of the iron subsystem in the spin-reorientation range depend on temperature much weaker.

Assuming $\mathbf{H} = 0$ in Eq. (1) and expanding thermodynamic potential (2) into a series in δH^i to an accuracy of second-order terms, we obtain the contribution of the paramagnetic gadolinium subsystem

$$K^{Gd}(T) = \alpha H_{exch} g\mu_B J B_J\left(\frac{g\mu_B J H_{exch}}{kT}\right) \equiv \alpha A(T), \quad (4)$$

where α is a small parameter on the order of $\delta H/H_{exch}$.

When an applied magnetic field is parallel to the c axis ($\mathbf{H} \parallel \mathbf{c}$), a spin-flop transition occurs in the gadolinium ferroborate [1, 3, 4]. The transition field depends on temperature, which is explained by the temperature-dependent contribution $K^{Gd}(T_{SF})$ of the rare-earth subsystem to the total anisotropy:

$$K^{Fe} + K^{Gd}(T_{SF}) = -\frac{\chi_\perp - \chi_\parallel}{2} H_{SF}^2, \quad (5)$$

where T_{SF} and H_{SF} are the temperature and magnetic field of the spin-flop transition, respectively, and $\chi_\perp$ and $\chi_\parallel$ are the transverse and longitudinal magnetic susceptibilities, respectively. With Eqs. (3)–(5), we can estimate K^{Fe} and α. Using the experimental data from [1, 3, 4],

$$T_{SR} = 10 \text{ K}, \quad H_{SF} = 8 \text{ kOe}, \quad T_{SF} = 4.2 \text{ K},$$
$$\chi_\perp - \chi_\parallel \approx 0.85\chi_\perp, \quad \chi_\perp \approx 15\mu_B/2H_E,$$
$$2H_E \approx 1.5 \times 10^6 \text{ Oe},$$

where H_E is the effective exchange field in the Fe system, we find

$$K^{Fe} = 15000\frac{\text{erg}}{\text{g}}, \quad \alpha \approx -0.004.$$

The authors of [1] detected a rather interesting new spin reorientation transition from the c axis toward the basal plane; it occurs at $T < T_{SR}$ in a magnetic field $\mathbf{H} \perp \mathbf{c}$. This is an unusual and unexpected transition, since, at first glance, there are no factors that could cause it: in both the initial easy-axis state ($\theta = 0$) and the final easy-plane state ($\theta = \pi/2$), the applied magnetic field is normal to the antiferromagnetism vector $\mathbf{L}$ (in the easy-plane phase, spins rotate freely in the plane; therefore, the condition $\mathbf{L} \cdot \mathbf{H} = 0$ is automatically satisfied even in very weak fields).

We can show that this behavior is caused by the fact that the contribution of the rare-earth subsystem to the anisotropy energy depends also on the applied magnetic field H. Assuming $H \neq 0$, $\mathbf{H} \perp \mathbf{c}$ in vector sum of fields (1) and expanding thermodynamic potential (2) into a series in δH^i to an accuracy of second-order

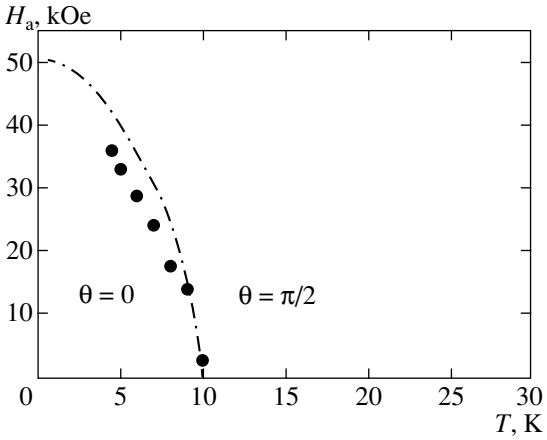

Fig. 2. *T–H* phase diagram of $GdFe_3(BO_3)_4$: (points) experimental and (curve) calculated dependences.

terms, we obtain the contribution of the paramagnetic gadolinium subsystem to the anisotropy:

$$K^{\mathrm{Gd}}(T, H) \approx \alpha \frac{g\mu_B J H_{\mathrm{exch}}^2}{\sqrt{H_{\mathrm{exch}}^2 + H^2}} \times B_J\left(\frac{g\mu_B J\sqrt{H_{\mathrm{exch}}^2 + H^2}}{kT}\right) \equiv \alpha A(T, H). \quad (6)$$

As for the consideration of the spontaneous spin-orientation transition at T_{SR} (Eq. (3)), the total anisotropy constant vanishes; however, we have to take into account field dependence (6). Actually, the $A(T, H)$ = const equation, which corresponds to the condition $K^{\mathrm{Gd}}(T, H) = -K^{\mathrm{Fe}}$, is the equation of the boundary separating the θ = 0 and π/2 phases in the *T–H* plane. As is seen from Fig. 2, at $g = 2$ and $H_{\mathrm{exch}} = 70$ kOe, Eq. (6) qualitatively explains the presence of the reverse transition: the magnetic field decreases the modulus of K^{Gd} and "restores" the crystal to the range of higher temperatures. The systematic deviation of experimental points from the theoretical curve toward lower critical H_c fields is likely to be related to the fact that Eq. (1) does not take into account the field of the dipole–dipole *f–d* interaction from the iron lattice; its consideration requires additional numerical calculations, namely, summation over the sites occupied by iron ions.

The magnetoelectric dependences of the rare-earth ferroborate $NdFe_3(BO_3)_4$ have another character (Fig. 1b). Unlike $GdFe_3(BO_3)_4$, the magnetoelectric properties of the neodymium ferroborate are mainly determined by the magnetic state of the rare-earth subsystem, which manifests itself in higher values of electric polarization (above 300 mC/m^2) and in an alternating character of the curves $P(H)$ (the dependences obtained were theoretically analyzed in detail in [2]). The shape of the magnetoelectric curves recorded when a magnetic field is applied along the *a*, *b*, and *c* axes also indicates that the magnetic moments of ions in the iron and rare-earth subsystems always lie in the basal plane.

To reveal the similarities and differences in the magnetic ordering of the gadolinium and neodymium ferroborates, we measured torque curves, since they are the best indicators of magnetic anisotropy and restructuring in the spin structures of the systems.

The shapes of the curves for $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$ shown in Fig. 3 indicate that, in a magnetic field at $T < T_{SR}$, the spins of the antiferromagnetic iron system in $GdFe_3(BO_3)_4$ reorient from the *c* toward the *a* axis and that, at $T > T_{SR}$, spins in $NdFe_3(BO_3)_4$ and $GdFe_3(BO_3)_4$ are always in the basal plane. The latter fact was then supported by spectral [10] and neutron diffraction [14] studies.

Thus, using a new family of magnetoelectrics, namely, rare-earth ferroborates, as an example, we revealed one of the possible mechanisms for magnetic control of electric polarization: magnetic-field-induced phase transitions cause electric polarization jumps.

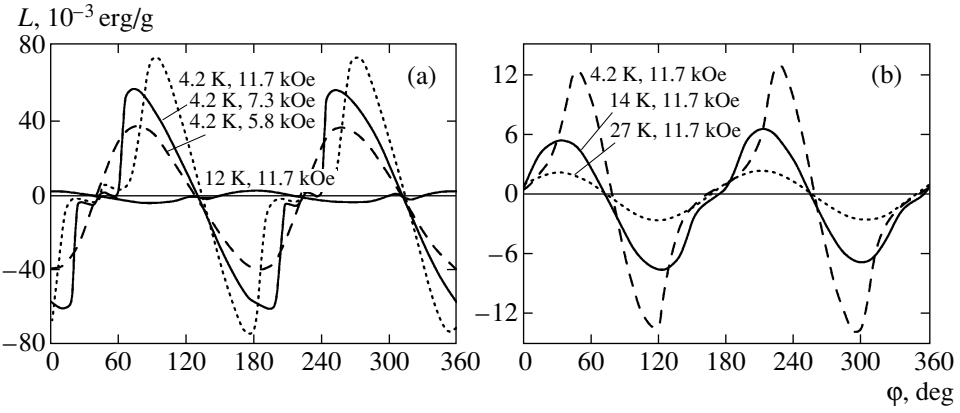

Fig. 3. Dependence of the torque on the angle in the *ac* plane for (a) $GdFe_3(BO_3)_4$ and (b) $NdFe_3(BO_3)_4$.

Spin transitions in the gadolinium ferroborate were thermodynamically analyzed.

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