

Observation of Spontaneous Spin Reorientation in $\text{Nd}_{1-x}\text{Dy}_x\text{Fe}_3(\text{BO}_3)_4$ Ferroborates with a Competitive R–Fe Exchange

Yu. F. Popov^a, A. M. Kadomtseva^a, G. P. Vorob'ev^a, A. A. Mukhin^b, V. Yu. Ivanov^b,
A. M. Kuz'menko^b, A. S. Prokhorov^b, L. N. Bezmaternykh^c, and V. L. Temerov^c

^a Moscow State University, Moscow, 119992 Russia

e-mail: Kadomts@plms.ru

^b Prokhorov General Physics Institute, Russian Academy of Sciences,
ul. Vavilova 38, Moscow, 119991 Russia

^c Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660038 Russia

Received February 26, 2009

The magnetic, magnetoelectric, and magnetoelastic properties of $\text{DyFe}_3(\text{BO}_3)_4$ single crystals and the $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ substituted compound with the competitive Nd–Fe and Dy–Fe exchange interactions have been investigated in magnetic fields up to 210 kOe. It has been shown that the antiferromagnetic state in $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ below the Néel temperature is easy-plane and a spontaneous spin-reorientation transition to a uniaxial state occurs near 25 K. Anomalies are observed in various physical characteristics in a spin-flop transition induced by the magnetic field along the trigonal axis. The H – T phase diagrams are constructed; they are in good agreement with a simple model taking into account the anisotropy of the exchange splitting and g factors of the ground doublets of the Dy^{3+} and Nd^{3+} ions. The features of the magnetoelectric effect in various magnetic phases have been studied. Spontaneous electric polarization has been revealed in the region of the existence of an easy-plane antiferromagnetic state in the substituted compound. A qualitative theoretical justification of the possibility of the appearance of the spontaneous spin-reorientation transition in the $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ substituted compound is given.

PACS numbers: 75.80.+q

DOI: 10.1134/S002136400907008X

The existence of magnetoelectric interactions in rare earth ferroborates, $\text{RFe}_3(\text{BO}_3)_4$, was recently revealed [1, 2]. A large advance has been achieved in studying the nature and manifestation of these interactions in various physical properties of these compounds. It has been shown that rare earth ferroborates belong to a new class of multiferroics in which the elastic, magnetic, and electric order parameters coexist.

Rare earth ferroborates have a rhombohedral structure and are described by the trigonal space group $R\bar{3}2(D_3^7)$ [3]. Below $T_N = 30$ – 40 K, the spins of Fe^{3+} are antiferromagnetically ordered and rare earth ions magnetized by the magnetic field of the iron subsystem are in a paramagnetic state. Below T_N , the spins of Fe^{3+} in ferroborates are ordered either in the ab plane of the crystal (easy-plane ferroborates) or along the c axis perpendicular to the ab plane (easy-axis ferroborates). The existence of easy-plane and easy-axis magnetic structures is apparently due to the difference in the ion radius and ground state of the rare earth ions

in these compounds. It was shown in [4–7] that the easy-plane magnetic structure is observed in neodymium ferroborate below $T_N \sim 32$ K, because it is preferable for Kramers magnetic ions Nd^{3+} ($^4I_{9/2}$). On the contrary, the easy-axis magnetic structure favorable for strongly anisotropic (but not Ising) ions Dy^{3+} ($^6H_{15/2}$) is observed in dysprosium ferroborate [8, 9].

It is of interest to analyze the competition between various contributions of Nd and Dy ions to the anisotropy of ferroborates when studying substituted compounds $\text{Nd}_{1-x}\text{Dy}_x\text{Fe}(\text{BO}_3)_4$ for which the appearance of spontaneous reorientation transitions from an easy-axis state to an easy-plane one can be reasonably expected. A similar spontaneous reorientation transition was previously observed in gadolinium ferroborate near 9 K [10, 11] and was explained by the anisotropy of the f – d exchange.

For such an analysis, the magnetic, magnetoelectric, and magnetoelastic properties were measured in pulsed magnetic fields up to 210 kOe and in static magnetic fields up to 12 kOe. A number of magnetic

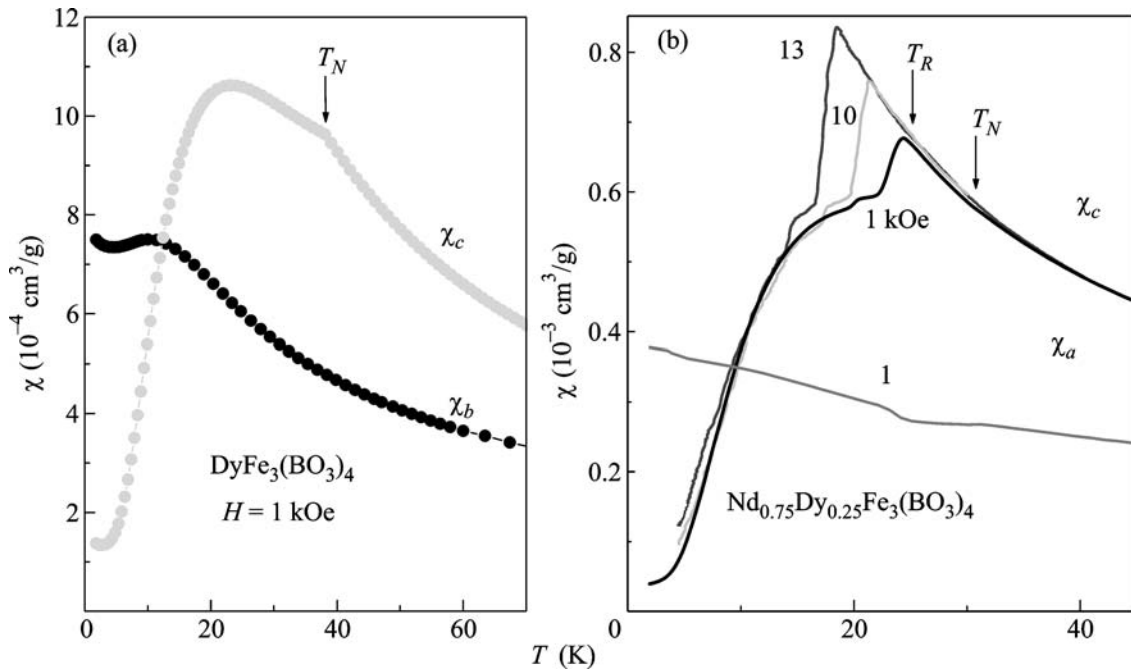


Fig. 1. Temperature dependences of the magnetic susceptibility along and perpendicular to the c axis in (a) $\text{DyFe}_3(\text{BO}_3)_4$ and (b) $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ measured in the fields indicated in the figure. The arrows mark the Néel temperature T_N and the reorientation transition temperature T_R .

measurements were performed on a SQUID magnetometer (MPMS-5 Quantum Design).

We investigate specially grown single crystals of $\text{DyFe}_3(\text{BO}_3)_4$ and $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ ferroborates for which the magnetoelastic and magnetoelectric properties have not yet been measured. A value of $x = 0.25$ for the substituted compound is chosen from the condition of the approximate equality of the contributions from various rare earth ions to anisotropy. It is assumed that the partial substitution of Nd^{3+} ions for Dy^{3+} ions leads not only to the appearance of the spin-reorientation transition, but also to a change in the magnitude of magnetoelectric interactions.

The single crystals of $\text{Nd}_{1-x}\text{Dy}_x\text{Fe}_3(\text{BO}_3)_4$ ($x = 1$ and 0.25) ferroborates were obtained using the spontaneous crystallization method from solutions in melts [12]. The methodical instructions for the measurements in pulsed magnetic fields were presented in our preceding work [13].

EXPERIMENTAL RESULTS

Figure 1a shows the temperature dependences of the magnetic susceptibility $\chi = \sigma/H$ (σ is the specific magnetization) measured on the SQUID magnetometer in a static magnetic field of 1 kOe along the b and c axes for pure dysprosium ferroborate at low temperatures (below 70 K). The dependences are rather complex. A cusp on the $\chi_c(T)$ curve at $T = 38$ K corresponds to a transition to the antiferromagnetic state

and the smooth maxima near 23 K along the c axis and near 11 K along the b axis are attributed to the Schottky effect associated with the redistribution of the populations of two low lying Kramers doublets of the Dy^{3+} ion. The same behavior of the magnetic susceptibility of $\text{DyFe}_3(\text{BO}_3)_4$ was recently observed in [9]. The significant decrease in χ_c at low temperatures confirms the uniaxial character of the magnetic anisotropy of dysprosium ferroborate. Figure 1b shows the $\chi(T)$ dependences for the substituted compound $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ in a field of $H = 1$ kOe along the a axis and in various magnetic fields along the c axis. As follows from the figure, an anomaly in the susceptibility at the Néel temperature $T_N \sim 32$ K in $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ is almost unobserved and the susceptibility along the c axis continues to increase with decreasing temperature; this behavior is characteristic of the easy-plane state. Then, a sharp decrease in χ_c occurs near 25 K, which can be attributed to the reorientation transition to the uniaxial state. An increase in the magnetic field applied along the c axis shifts this transition towards lower temperatures.

Figure 2a shows the magnetization curves of dysprosium ferroborate measured on the SQUID magnetometer in fields up to 50 kOe; the inset in this figure shows the field dependences of magnetization in pulsed fields up to 130 kOe. According to the figure, magnetization jumps appear in a sufficiently high magnetic field H_{cr} along the c axis of the crystal; these jumps are associated with spin-flop transitions in the

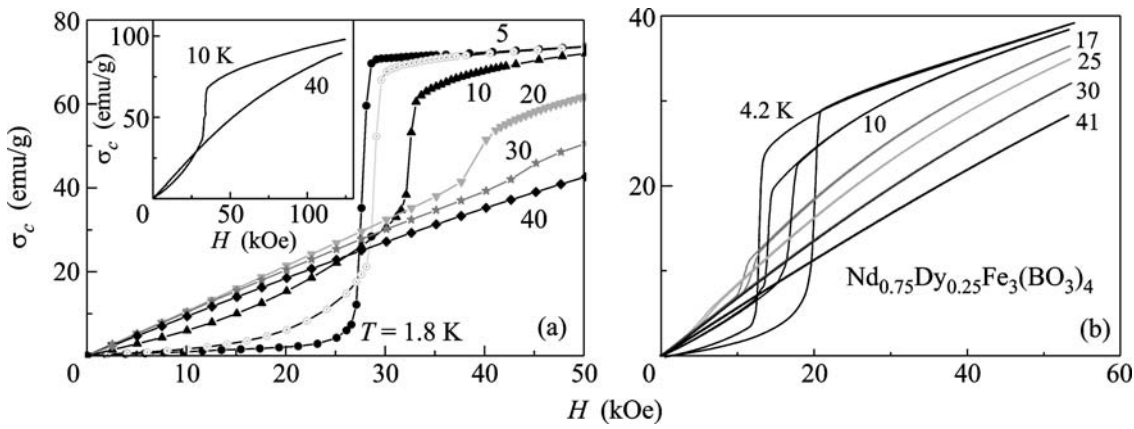


Fig. 2. Magnetization curves along the c axis in (a) $\text{DyFe}_3(\text{BO}_3)_4$ measured on the SQUID magnetometer (in the inset, in pulsed fields) and (b) $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ measured in pulsed magnetic fields.

iron sublattice and the threshold fields of the transition increase with temperature. The magnetic moments of the Dy^{3+} ions are simultaneously reoriented to the direction parallel to the magnetic field, which ensures a large magnetization jump. Our $\sigma(H)$ dependences are in good agreement with the magnetization curves from [9].

Figure 2b shows the magnetization curves for the substituted compound $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$, which exhibit a stepwise increase in the magnetization in the spin-flop transition for $H \parallel c$ only in a low-temperature range of 4.2–25 K, whereas the $\sigma_c(H_c)$ dependences above 25 K are monotonic. These data confirm the conclusion following from the $\chi(T)$ dependences that the spontaneous spin-reorientation transition from the c axis to the basal plane occurs at a temperature of $T_R \sim 25$ K.

The measurement of the pyroelectric current shows that spontaneous electric polarization with the components along the a and b axes of the crystal appears in substituted dysprosium ferroborate below $T_N \sim 32$ K (see Fig. 3). Near the spin-reorientation transition temperature, the behavior of this spontaneous polarization is complex and it disappears at lower temperatures corresponding to the uniaxial state. Typical values of spontaneous polarization are several microcoulombs per square meter. The appearance of polarization is possibly attributed to the reduction of the symmetry of the highly symmetric crystalline phase $R32 (D_3^7)$ due to elastic stresses (distortions) in the crystal lattice in the substituted compound, which can discriminate a certain dominant orientation of spins in the basal plane, thus violating the uniform distribution of spins over 120° domains.

It is found that the spin-flop transition for $H \parallel c$ in $\text{DyFe}_3(\text{BO}_3)_4$ and $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ is accompanied not only by the magnetization jump, but also by sharp anomalies in all components of the electric

polarization, $\Delta P_i \sim 10 \mu\text{C}/\text{m}^2$ ($i = a, b, c$), and magnetostriction, $\Delta \lambda_i \sim 10^{-6}$; in the substituted compound, these anomalies are observed only at temperatures below T_R . Figures 4 and 5 show the field dependences of the longitudinal electric polarization and magnetostriction along the c axis of the $\text{DyFe}_3(\text{BO}_3)_4$ and $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ crystals. For the $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ single crystal at temperatures above $T_R \sim 25$ K that correspond to the easy-plane state, polarization anomalies are also observed in sufficiently weak magnetic fields ($H_{cr} \sim 5$ kOe) applied in the basal plane. These anomalies can be attributed to the reorientation of spins (antiferromagnetic moment) of the Fe^{3+} ions to the direction perpendicular to the field (see Fig. 6). The quadratic magnetoelectric polarization in the ab plane in the substituted compound in fields ~ 100 kOe reaches $\sim 200 \mu\text{C}/\text{m}^2$, which exceeds the polarization of the majority of pure ferro-

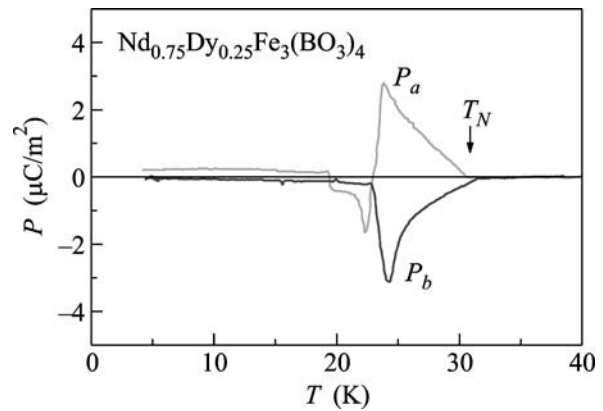


Fig. 3. Temperature dependences of spontaneous electric polarization along the a and b axes of the $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ single crystal.

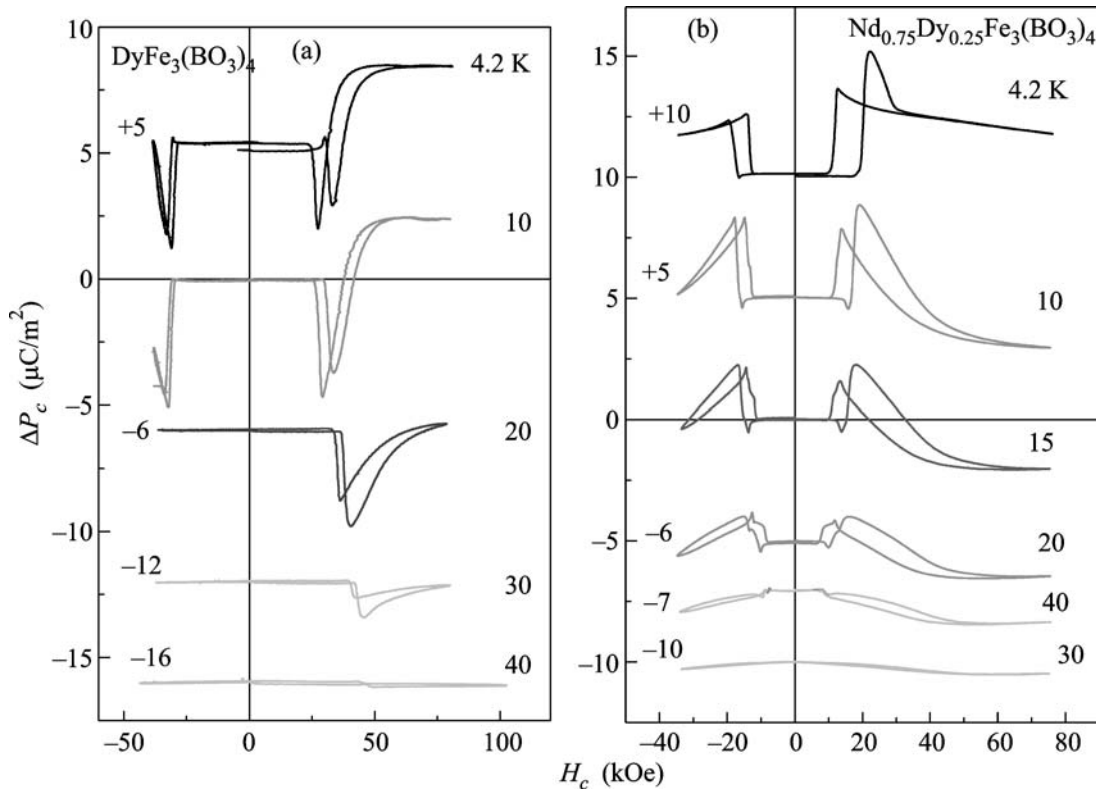


Fig. 4. Field dependences of longitudinal electric polarization along the c axis in (a) $\text{DyFe}_3(\text{BO}_3)_4$ and (b) $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ at various temperatures indicated to the right of the lines. The shifts of the lines along the ordinate axis are indicated to the left of the lines.

borates, but is lower than that observed in $\text{NdFe}_3(\text{BO}_3)_4$. The replacement of Nd ions by Dy ions that have a larger magnetic moment does not lead to the expected increase in the magnetoelectric effect, which is probably associated with a small contribution from Dy^{3+} ions to the magnetic and magnetoelectric properties in the ab plane, as well as with the appearance of crystallographic distortions accompanying the replacement of Nd ions by ions with a smaller ion radius.

The temperature dependences of the threshold fields of the ferroborates under consideration for $H \parallel c$ obtained by measuring the magnetic and magnetoelectric properties and magnetostriction are shown in Fig. 7. The threshold fields in $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ are smaller than those in $\text{DyFe}_3(\text{BO}_3)_4$ and decrease strongly with increasing temperature and vanish near the spontaneous spin-reorientation transition temperature $T_R \approx 25$ K.

The observed properties of the rare earth ferroborates can be qualitatively explained on the basis of the following thermodynamic potential of the system:

$$\Phi(\mathbf{l}) = -\frac{1}{2}\chi_{\perp}^{\text{Fe}}\mathbf{H}^2 + (\chi_{\perp}^{\text{Fe}} - \chi_{\parallel}^{\text{Fe}})(\mathbf{H}\mathbf{l})^2 + \frac{1}{2}K_{\text{Fe}}l_z^2$$

$$-\frac{1}{2}(1-x)Nk_B T \sum_{\alpha=\pm} \ln[2 \cosh(\Delta_{\text{Nd}}^{\alpha}/k_B T)] \quad (1)$$

$$-\frac{1}{2}xNk_B T \sum_{\alpha=\pm} \ln[2 \cosh(\Delta_{\text{Dy}}^{\alpha}/k_B T)].$$

Here, the first three terms determine the contribution from the antiferromagnetically ordered Fe subsystem and the last two terms specify the contribution from rare earth ions Dy^{3+} and Nd^{3+} , which are considered in the single-doublet approximation; $\mathbf{l} = (l_{\perp}, l_z)$ is the dimensionless antiferromagnetic vector of iron ions; χ_{\perp}^{Fe} and $\chi_{\parallel}^{\text{Fe}}$ are the transverse and longitudinal susceptibilities of the Fe subsystem, respectively; $K_{\text{Fe}} > 0$ is the uniaxial anisotropy constant of the Fe subsystem; and $2\Delta_{\text{R}}^{\pm}$ are the splittings of the ground doublet of the ions $\text{R} = \text{Dy}$ and Nd ,

$$\Delta_{\text{R}}^{\pm} = [(\mu_{\text{R}}^z H_z \pm \Delta_{\text{R}}^z l_z)^2 + (\mu_{\text{R}}^{\perp} H_{\perp} \pm \Delta_{\text{R}}^{\perp} l_{\perp})^2]^{1/2}, \quad (2)$$

where μ_{R}^z and μ_{R}^{\perp} are the magnetic moments of the ions along and perpendicular to the $z(c)$ axis, respec-

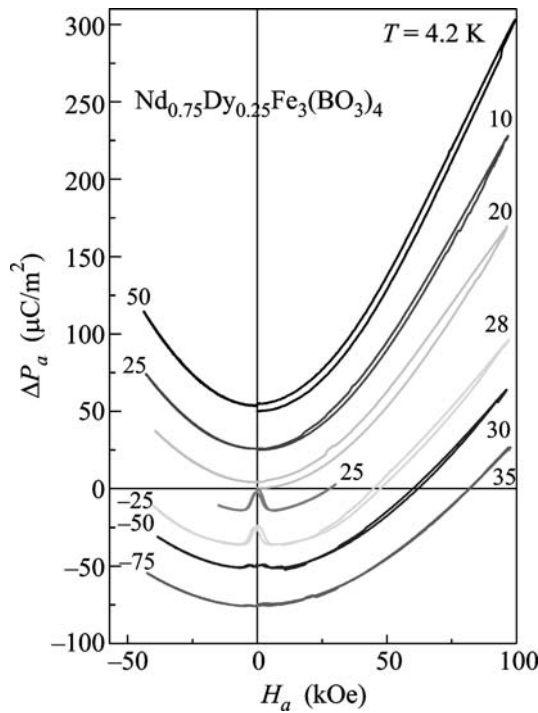


Fig. 6. Field dependences of longitudinal electric polarization in $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ measured for $H \parallel a$.

tial thermodynamic potential (1) (taking into account the inequality $\mu_{\text{Nd}}^z H_{\text{sf}}, \Delta_{\text{Nd}}^z \ll \Delta_{\text{Nd}}^\perp$):

$$H_{\text{sf}} \approx \left[xN\Delta_{\text{Dy}}^z - (1-x)N\Delta_{\text{Nd}}^\perp - \frac{1}{2}K_{\text{Fe}} \right] / xN\mu_{\text{Dy}}^z. \quad (5)$$

It follows from this expression that the field H_{sf} in pure $\text{DyFe}_3(\text{BO}_3)_4$ is close to the exchange splitting field of the ground doublet of Dy^{3+} , $\Delta_{\text{Dy}}^z / \mu_{\text{Dy}}^z$, and the spin-flop field in the mixed compound decreases noticeably due to the Nd subsystem in good agreement with experiment (see Fig. 7).

Thus, this model taking into account the anisotropy of the exchange splitting and g factors of the ground doublets of the Dy^{3+} and Nd^{3+} ions describes the observed phase transitions in the $\text{Nd}_{1-x}\text{Dy}_x\text{Fe}_3(\text{BO}_3)_4$ system with competitive rare earth contributions.

To summarize the results of the work, we note that a spontaneous spin-reorientation transition from the c axis to the ab plane is implemented in a single crystal of substituted ferroborate $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ due to the competition between different contributions to magnetic anisotropy. The investigation of the reorientation transitions induced by the magnetic field reveals anomalies in the closely correlated magnetic, magnetoelastic, and magnetoelectric properties for both compounds. The H - T phase diagrams have significantly different forms for $\text{DyFe}_3(\text{BO}_3)_4$ and

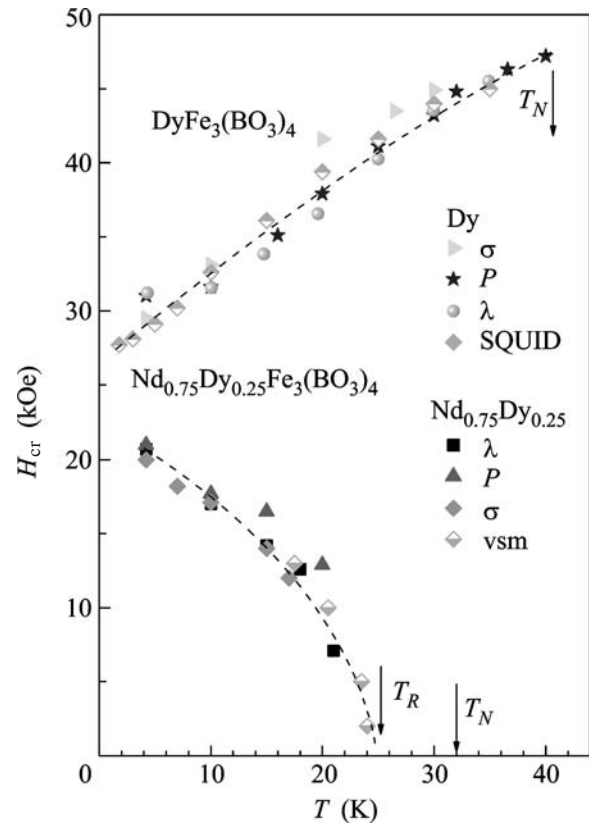


Fig. 7. Temperature dependences of the threshold field of the spin-flop transition in (a) $\text{DyFe}_3(\text{BO}_3)_4$ and (b) $\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$ obtained from the measurements of magnetization (σ), magnetostriction (λ), and electric polarization (ΔP) in pulsed magnetic fields, as well as the magnetization measured in static fields on the vibrating sample magnetometer (vsm) and SQUID magnetometer (SQUID). The arrows mark the Néel temperature T_N and the reorientation transition temperature T_R .

$\text{Nd}_{0.75}\text{Dy}_{0.25}\text{Fe}_3(\text{BO}_3)_4$; these diagrams are theoretically explained.

We are deeply grateful to A.K. Zvezdin and A.P. Pyatakov for useful advice and to E.A. Popova for placing the $\text{DyFe}_3(\text{BO}_3)_4$ single crystal at our disposal. This work was supported by the Russian Foundation for Basic Research (project no. 07-02-00580-a).

REFERENCES

1. A. K. Zvezdin, S. S. Krotov, A. M. Kadomtseva, et al., Pis'ma Zh. Eksp. Teor. Fiz. **81**, 335 (2005) [JETP Lett. **81**, 272 (2005)].
2. A. K. Zvezdin, G. P. Vorob'ev, A. M. Kadomtseva, et al., Pis'ma Zh. Eksp. Teor. Fiz. **83**, 600 (2006) [JETP Lett. **83**, 509 (2006)].
3. S. A. Klimin, D. Fausti, and A. Meetsma, Acta Crystallogr. B **61**, 481 (2005).
4. E. P. Chukalina, D. Y. Kurtisin, and M. N. Popova, Phys. Lett. A **322**, 239 (2004).

5. P. Fischer, V. Pomjakushin, and D. Sheptyakov, *J. Phys.: Condens. Matter* **18**, 7975 (2006).
6. E. P. Popova, N. Tristan, Kh. Khess, et al., *Zh. Eksp. Teor. Fiz.* **132**, 121 (2007) [*JETP* **105**, 105 (2007)].
7. A. M. Kadomtseva, A. K. Zvezdin, and A. P. Pyatakov, *Zh. Eksp. Teor. Fiz.* **132**, 134 (2007) [*JETP* **105**, 116 (2007)].
8. T. N. Stanislavchuk, E. P. Chukalina, et al., *Phys. Lett. A* **368**, 408 (2007).
9. E. A. Popova, N. Tristan, and A. N. Vasiliev, *Eur. Phys. J. B* **62**, 123 (2008).
10. A. D. Balaev, I. N. Bezmaternikh, and I. A. Gudim, *J. Magn. Magn. Mater.* **258–259**, 532 (2003).
11. A. I. Pankrats, G. A. Petrakovsky, L. N. Bezmaternykh, and O. A. Bayukov, *Zh. Eksp. Teor. Fiz.* **126**, 887 (2004) [*JETP* **99**, 766 (2004)].
12. L. N. Bezmaternykh, S. A. Kharlamov, and V. L. Temmerov, *Kristallografiya* **49**, 1 (2004) [*Crystallogr. Rep.* **49**, 855 (2004)].
13. A. K. Zvezdin, A. M. Kadomtseva, Yu. F. Popov, et al., *Zh. Eksp. Teor. Fiz.* (2009, in press).
14. D. V. Volkov, A. A. Demidov, and N. P. Kolmakova, *Zh. Eksp. Teor. Fiz.* **133**, 830 (2008) [*JETP* **106**, 723 (2008)].

Translated by R. Tyapaev