

# Effects of the Interaction between R and Fe Modes of the Magnetic Resonance in $\text{RFe}_3(\text{BO}_3)_4$ Rare-Earth Iron Borates

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Received June 3, 2011

Resonance modes that are due to magnetic excitations in the exchange-coupled subsystems of rare-earth ions ( $\text{R} = \text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ , and  $\text{Gd}^{3+}$ ) and  $\text{Fe}^{3+}$  ions have been detected in submillimeter transmission spectra (0.1–0.6 THz) of  $\text{RFe}_3(\text{BO}_3)_4$  iron borate–multiferroic single crystals. The strong interaction between spin oscillations of the Fe and R subsystems has been revealed, which determines the behavior of the modes depending on the anisotropy of the exchange splitting of the ground doublet of the R ion. It has been shown that the intensities of coupled modes (contributions to the magnetic permeability) depend strongly on the difference between the  $g$  factors of Fe and R ions. This dependence makes it possible to determine the sign of the latter  $g$  factor. In particular, a noticeable intensity of exchange Nd modes in  $\text{NdFe}_3(\text{BO}_3)_4$  is due to an increase in their contribution at  $g_{\perp, \parallel}^{\text{Nd}} < 0$ , while in  $\text{GdFe}_3(\text{BO}_3)_4$  with  $g_{\text{Gd}} \approx g_{\text{Fe}} \approx 2$ , the Fe and Gd contributions compensate each other and the exchange (Gd) mode is not observed. In spite of the weak interaction of Sm ions with the magnetic field,  $\text{SmFe}_3(\text{BO}_3)_4$  exhibits resonance modes, which are attributed to the excitation of Sm ions through the Fe subsystem.

DOI: 10.1134/S0021364011160119

## 1. INTRODUCTION

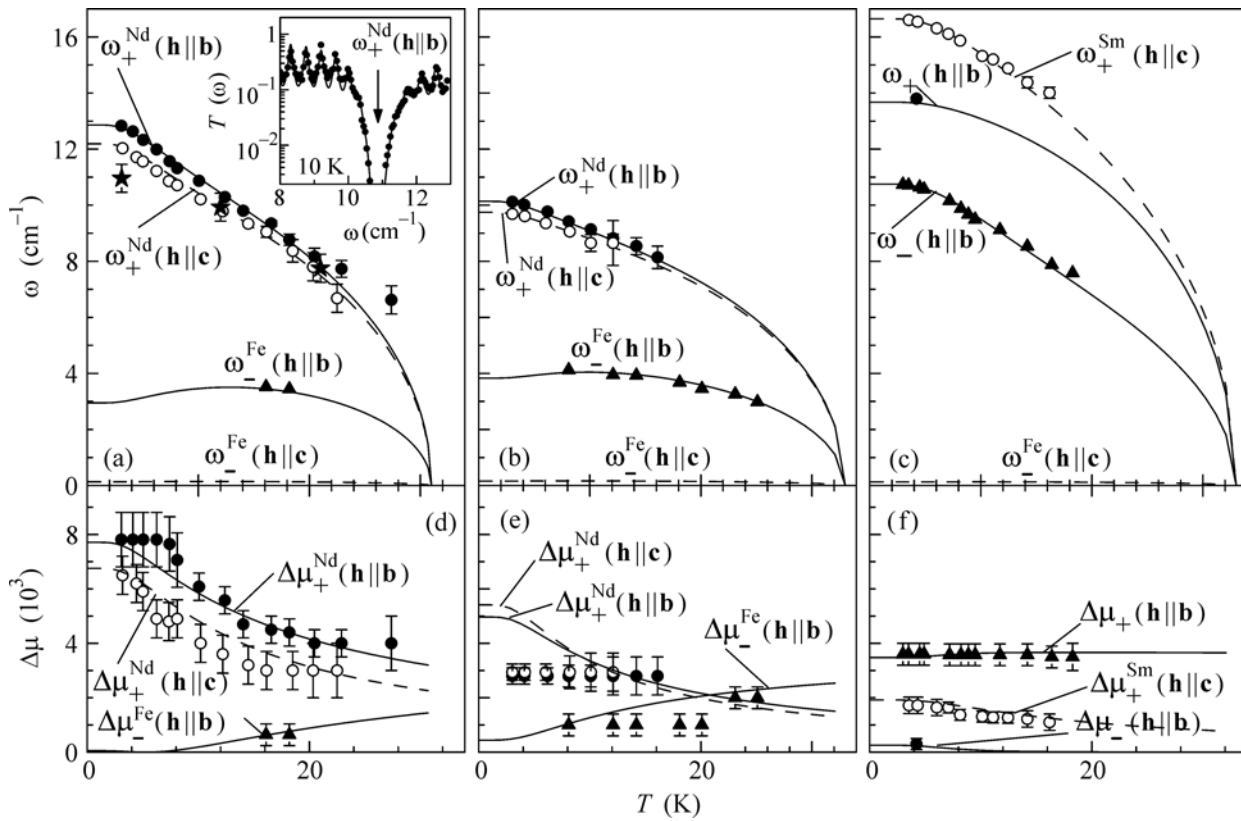
Among various magnetoelectric materials that have been actively studied in recent years [1–4], rare-earth iron borates  $\text{RFe}_3(\text{BO}_3)_4$  attract significant attention [5–8] due to their interesting magnetic, optical, and multiferroelectric properties resulted from the exchange interaction between the iron and rare-earth magnetic subsystems. They have a noncentrosymmetric trigonal structure (space group  $R\bar{3}2$  or  $P3_121$ ) [9–11]. The antiferromagnetic ordering of  $\text{Fe}^{3+}$  ions occurs in them below  $T_N \sim 30$ –40 K. The spins of iron are oriented either along the trigonal  $c$  axis (easy-axis structure) or in the basal  $ab$  plane (easy-plane structure). The magnetic order is also induced in the R subsystem due to the R–Fe exchange, which is of primary importance in the stabilization of a certain magnetic structure and in the formation of magnetic and magnetoelectric properties.

These features of the interacting Fe and R subsystems should be manifested not only in static magnetic and magnetoelectric properties, but also in high-frequency magnetic resonance phenomena; study of these phenomena began only recently [12–14]. In particular, the strong effect of R ions on the modes of the antiferromagnetic resonance of the Fe subsystem in the submillimeter wavelength range was revealed in Tb, Pr, and Eu iron borates [14]. This effect was man-

ifested in an additional contribution to the anisotropy energy (in Eu iron borate) and in a change in its sign (in Pr and Tb iron borates), which was clearly seen in the behavior of the frequencies of antiferromagnetic resonance. These frequencies were much lower than the characteristic frequencies of electron transitions in these R ions. However, according to optical data, splittings of lower doublets of many R ions in the exchange R–Fe field ( $\Delta_{\text{Nd}} = 8.8 \text{ cm}^{-1}$  [15],  $\Delta_{\text{Sm}} = 13.2 \text{ cm}^{-1}$  [16]) are in the submillimeter frequency range and have transition frequencies comparable with the frequencies of antiferromagnetic resonance of the Fe subsystem (4–15  $\text{cm}^{-1}$ ) [13, 14]. For this reason, the magnetic resonance properties of these iron borates should be determined by coupled oscillations of the spins of Fe and R subsystems. The aims of this work are to detect and study these excitations.

## 2. EXPERIMENT

Iron borate single crystals with  $\text{R} = \text{Nd}$ ,  $\text{Sm}$ , and  $\text{Gd}$ , as well as substituted compounds on their basis with  $\text{R} = \text{Nd}_{0.4}\text{Y}_{0.6}$ ,  $\text{Gd}_{0.96}\text{Nd}_{0.04}$ ,  $\text{Gd}_{0.75}\text{Nd}_{0.25}$ , and  $\text{Gd}_{0.5}\text{Nd}_{0.5}$ , were grown by the method of crystallization from a melt on seeds [17]. The samples were prepared in the form of plane–parallel  $a$ -cut plates with the transverse sizes up to 1 cm and a thickness of about

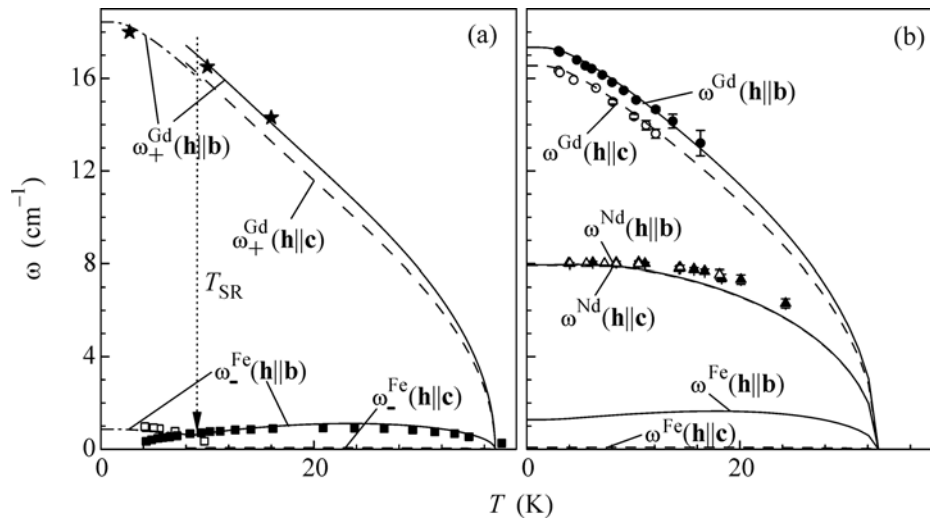


**Fig. 1.** Temperature dependences of (a–c) frequencies and (d–f) contributions to the magnetic permeability of the resonance modes ( $\mathbf{h} \parallel \mathbf{b}$ ,  $\mathbf{h} \parallel \mathbf{c}$ ) in (a, d)  $\text{NdFe}_3(\text{BO}_3)_4$ , (b, e)  $\text{Nd}_{0.4}\text{Y}_{0.6}\text{Fe}_3(\text{BO}_3)_4$ , and (c, f)  $\text{SmFe}_3(\text{BO}_3)_4$ . Circles and triangles denote the submillimeter transmission spectral data, stars are the data from Raman spectra [10], and lines are theoretical calculations. The inset shows the transmission spectrum near the  $\omega_-^{\text{Nd}}(\mathbf{h} \parallel \mathbf{b})$  mode, where points are experimental data and the line is the simulation.

1 mm. The polarization transmission spectra  $T(\nu)$  were measured using the quasi-optical backward-wave oscillator spectroscopy [18] in the frequency range of 3–20  $\text{cm}^{-1}$  at temperatures 3–300 K. In the antiferromagnetic ordering range ( $T < T_N = 35\text{--}40$  K), resonance lines were revealed in the spectra (inset in Fig. 1a). These resonance lines were observed at the polarizations of the magnetic field  $\mathbf{h} \parallel \mathbf{b}$  and  $\mathbf{h} \parallel \mathbf{c}$  and were identified as magnetic excitations in the Fe and R subsystems (see below). The spectra were simulated using the Fresnel formulas for a plane-parallel layer taking into account the dispersion of the magnetic susceptibility  $\mu(\omega) = 1 + \sum_k \Delta\mu_k \omega_k^2 / (\omega_k^2 - \omega^2 + i\omega\Delta\omega_k)$ , where  $\omega_k$ ,  $\Delta\omega_k$ , and  $\Delta\mu_k$  are the frequency, linewidth, and the contribution to the permeability of the  $k$ th mode, respectively.

In all of the compounds under investigation, the easy-plane antiferromagnetic structure occurs below the Néel point. Resonance lines for  $\text{NdFe}_3(\text{BO}_3)_4$  are observed for both magnetic field polarizations  $\mathbf{h} \parallel \mathbf{b}$  and  $\mathbf{h} \parallel \mathbf{c}$  (Fig. 1a) unlike the easy-plane compounds  $\text{YFe}_3(\text{BO}_3)_4$  and  $\text{EuFe}_3(\text{BO}_3)_4$  [14], where only high-

frequency mode of antiferromagnetic resonance of iron ions at  $\mathbf{h} \parallel \mathbf{b}$  at frequencies of 4–6  $\text{cm}^{-1}$  was observed. The appearance of two resonance lines at frequencies of about 12  $\text{cm}^{-1}$  in  $\text{NdFe}_3(\text{BO}_3)_4$  at two different polarizations is apparently due to the excitations of electronic transitions in ground Kramers doublet of the  $\text{Nd}^{3+}$  ion, which is split by the exchange Nd–Fe interaction. However, the observed frequencies are much higher than an exchange splitting of about 8.8  $\text{cm}^{-1}$  that was obtained from optical data [15]. In addition, attributes of a weak line for  $\mathbf{h} \parallel \mathbf{b}$ , which can be identified as a high-frequency mode of the antiferromagnetic resonance in the Fe subsystem, were revealed at a frequency of about 3.5  $\text{cm}^{-1}$ . The contribution to the magnetic permeability from this mode is much smaller than the contribution observed in the  $\text{YFe}_3(\text{BO}_3)_4$  and  $\text{EuFe}_3(\text{BO}_3)_4$  compounds [14]. The behavior of the resonance frequencies (repulsion), together with the redistribution of the contributions (intensities) of the modes, indicates a strong coupling of the spin oscillations of Fe and Nd subsystems.



**Fig. 2.** Temperature dependences of the resonance frequencies in (a)  $\text{GdFe}_3(\text{BO}_3)_4$  and (b)  $\text{Gd}_{0.5}\text{Nd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  iron borates. Stars are Raman data from [10], squares are the antiferromagnetic resonance data from [12, 13], circles and triangles are data obtained in this work, and lines are theoretical calculations. The arrow indicates the spin reorientation temperature  $T_{\text{SR}}$ .

The results obtained when Nd is diluted by non-magnetic Y in  $\text{Nd}_{0.4}\text{Y}_{0.6}\text{Fe}_3(\text{BO}_3)_4$  (Fig. 1b) confirm this character of spin excitations. It can be seen that, as the Nd concentration decreases, the frequencies of high-frequency (Nd) modes decrease at both polarizations and become closer to the static exchange splitting of the ground  $\text{Nd}^{3+}$  doublet and the frequency of the antiferromagnetic resonance mode approaches the value for yttrium iron borate. This indicates a decrease in the interaction between the antiferromagnetic resonance and R modes upon dissolution. Note that this separation of modes into rare-earth and antiferromagnetic resonance ones is very conditional, because coupled oscillations of Fe and R spins occur, which will be discussed in detail below.

The feature of the  $\text{SmFe}_3(\text{BO}_3)_4$  compound is that the  $\text{Sm}^{3+}$  ion has very small Landé factor and makes an insignificant contribution to the static magnetic properties [8], which are similar to  $\text{YFe}_3(\text{BO}_3)_4$ . Nevertheless, the role of  $\text{Sm}^{3+}$  ions is strongly manifested in the submillimeter properties. Resonance modes were revealed for both polarizations (Fig. 1c). For  $\mathbf{h} \parallel \mathbf{c}$ , when the low-frequency mode of antiferromagnetic resonance, which is much lower than the range under investigation, is usually excited, we observed a pronounced mode with a frequency of about  $16.6 \text{ cm}^{-1}$  at low temperatures. This mode can be attributed to electronic transitions inside the Kramers doublet of  $\text{Sm}^{3+}$ . The fact that its frequency is higher than the exchange splitting of the doublet  $\Delta_{\text{Sm}} = 13.2 \text{ cm}^{-1}$  [16] is apparently due to the interaction (repulsion) with the low-lying antiferromagnetic resonance mode. It is surprising that the Sm mode has a noticeable intensity in spite of the weak interaction of  $\text{Sm}^{3+}$  ions with the magnetic field (see the contribution  $\Delta\mu_+(\mathbf{h} \parallel \mathbf{c})$  in

Fig. 1f). This can be attributed to the excitation of electronic transitions in  $\text{Sm}^{3+}$  through the Fe subsystem due to their exchange interaction (see below). For another polarization,  $\mathbf{h} \parallel \mathbf{b}$ , two modes are observed, one of which (with a lower frequency) was clearly manifested in a wide temperature range, while the other mode had a much smaller intensity and was only manifested at low temperatures. The appearance of these modes is apparently due to the coupled oscillations of the spins of  $\text{Fe}^{3+}$  and  $\text{Sm}^{3+}$ . Note that the repulsion of the frequencies is manifested insignificantly for these modes.

Other iron borates that surprisingly exhibit resonance properties are  $\text{GdFe}_3(\text{BO}_3)_4$  and a number of substituted compounds based on it. In pure  $\text{GdFe}_3(\text{BO}_3)_4$ , a spontaneous spin-reorientation transition from the easy-plane to uniaxial state occurs at  $T_{\text{R}} \sim 9 \text{ K}$  [19] due to the competition between the contributions from the Fe and Gd subsystems to the anisotropy energy. According to [13], the high-frequency mode of the antiferromagnetic resonance of the Fe subsystem does not exceed  $1 \text{ cm}^{-1}$  (30 GHz) and is softer near  $T_{\text{R}}$ . According to the estimate of the Gd–Fe exchange field ( $\sim 70 \text{ kOe}$ ) based on the static properties [20], the characteristic frequencies (level splittings of about  $6.5 \text{ cm}^{-1}$ ) of the Gd subsystem should be much higher and should lie in our frequency range. We tried to detect Gd modes in the submillimeter range in  $\text{GdFe}_3(\text{BO}_3)_4$ . However, we have found no resonance excitations. At the same time, Gd modes in the substituted compound  $\text{Gd}_{0.5}\text{Nd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  were clearly manifested along with Nd modes for both polarizations at frequencies much higher than the static splitting of the levels of  $\text{Gd}^{3+}$  ions (Fig. 2b).

### 3. THEORY AND DISCUSSION OF THE RESULTS

To describe the observed magnetic resonance properties of iron borates, we use the nonequilibrium thermodynamic potential of the system  $\Phi = \Phi_{\text{Fe}} + \Phi_{\text{R}}$ . In the two-sublattice approximation, the thermodynamic potential of the Fe subsystem can be represented in the form [20, 21]

$$\Phi_{\text{Fe}}(\mathbf{M}, \mathbf{L}) = \Phi_0(\mathbf{L}) + \frac{1}{2}A\mathbf{M}^2 - M_0\mathbf{M}\mathbf{H} + \frac{1}{2}K_{A2}L_z^2 - \frac{1}{12}K_{A6}[(L_x + iL_y)^6 + (L_x - iL_y)^6], \quad (1)$$

where  $\mathbf{M}$  and  $\mathbf{L}$  are the ferromagnetic and antiferromagnetic vectors, respectively;  $A = 2H_E M_0 = M_0^2/\chi_{\perp}$  is the isotropic Fe–Fe exchange constant;  $H_E$  is the corresponding exchange field;  $\chi_{\perp}$  is the transverse magnetic susceptibility of iron;  $K_{A2} > 0$  is the anisotropy constant that stabilizes the easy-plane antiferromagnetic state;  $K_{A6}$  is the anisotropy constant in the  $ab$  basal plane ( $|K_{A6}| \ll K_{A2}$ );  $M_0 \approx 3g_{\text{Fe}}S_{\text{Fe}}\mu_{\text{B}}N$  is the saturation magnetic moment of the Fe subsystem; and  $\Phi_0(\mathbf{L})$  is the exchange part of the thermodynamic potential, which determine the length of the vector  $\mathbf{L}$ .

We describe the R subsystem in the single-doublet approximation using the effective spin Hamiltonian [22]

$$H_{\text{R}}^{(1,2)} = -\hat{\sigma}_{1,2}\mathbf{h}_{\text{eff}1,2} \equiv -\hat{\sigma}_{1,2}(\hat{\mu}\mathbf{H} + \hat{a}\mathbf{M} \pm \hat{b}\mathbf{L}), \quad (2)$$

where  $\hat{\sigma}_1$  and  $\hat{\sigma}_2$  are the Pauli matrices of the ground doublet for R ions in sublattices 1 and 2, respectively;  $\mathbf{h}_{\text{eff}1,2}$  is the effective field [6, 20, 21] in which the magnetic moment  $\hat{\mu} = \frac{1}{2}\hat{g}\mu_{\text{B}}$  is determined by the  $g$  tensor

of the doublet ( $g_{xx} = g_{yy} \equiv g_{\perp}$ ,  $g_{zz} \equiv g_{\parallel}$ ); and  $\hat{a}$  and  $\hat{b}$  are the diagonal matrices of R–Fe exchanges ( $a_{xx} = a_{yy} \equiv a_{\perp}$ ,  $a_{zz} \equiv a_{\parallel}$ ;  $b_{xx} = b_{yy} \equiv b_{\perp}$ ,  $b_{zz} \equiv b_{\parallel}$ ). In the nearest neighbor approximation,  $\hat{a} = \hat{b}$ . The average Pauli matrices  $\sigma_{1,2} \equiv \langle \hat{\sigma}_{1,2} \rangle$  or their linear combinations  $\mathbf{m} = (\sigma_1 + \sigma_2)/2$  and  $\mathbf{l} = (\sigma_1 - \sigma_2)/2$  are used as the dynamic variables of the R subsystem. The rare-earth part of the thermodynamic potential, which is due to the ground doublet, can be represented in the form (molecular field approximation) [22]

$$\Phi_{\text{R}} = N \left[ -\mathbf{m}(\hat{\mu}\mathbf{H} + \hat{a}\mathbf{M}) - \mathbf{l}\hat{b}\mathbf{L} - \frac{1}{2}k_{\text{B}}T \sum_{i=1,2} S(\sigma_i) \right], \quad (3)$$

where  $S(\sigma) = \ln 2 - \frac{1}{2}(1 + \sigma)\ln(1 + \sigma) - \frac{1}{2}(1 - \sigma)\ln(1 - \sigma)$  is the entropy of the two-level system and  $N$  is the number of R ions. The contribution of the excited

states of the R ion can be taken into account by the renormalization of  $\Phi_{\text{Fe}}$ . The equilibrium state of the system is determined from the condition of the minimum of  $\Phi$ . At  $\mathbf{H} = 0$ , when  $\mathbf{M} = \mathbf{m} = 0$ , the equilibrium value  $\mathbf{l} = (\mathbf{L}/L)\tanh(|\hat{b}\mathbf{L}|/k_{\text{B}}T)$  is certainly related to  $\mathbf{L}$ . The dynamics of the Fe and R subsystem is described by the Landau–Lifshitz equations [23]

$$\begin{aligned} (M_0/\gamma_{\text{Fe}})\dot{\mathbf{M}} &= [\mathbf{M}\Phi_{\text{M}}] + [\mathbf{L}\Phi_{\text{L}}], \\ (M_0/\gamma_{\text{Fe}})\dot{\mathbf{L}} &= [\mathbf{M}\Phi_{\text{L}}] + [\mathbf{L}\Phi_{\text{M}}], \\ (m_0/\gamma)\dot{\mathbf{m}} &= [\mathbf{m}\Phi_{\text{m}}] + [\mathbf{l}\Phi_{\text{l}}], \\ (m_0/\gamma)\dot{\mathbf{l}} &= [\mathbf{m}\Phi_{\text{l}}] + [\mathbf{l}\Phi_{\text{m}}], \end{aligned} \quad (4)$$

where  $\Phi_{\text{M}} = \partial\Phi/\partial\mathbf{M}$ , etc.,  $m_0 = \mu_{\text{B}}N$ ,  $\gamma_{\text{Fe}} = g_{\text{Fe}}\mu_{\text{B}}/\hbar$ , and  $\gamma = 2\mu_{\text{B}}/\hbar$ . We consider spin oscillations of the system in the easy-plane state  $\mathbf{L} \perp \mathbf{c}$ , taking  $\mathbf{L} = (L_x, 0, 0)$  and  $\mathbf{l} = (l_x, 0, 0)$  for certainty, which is stabilized at  $K_{A6} > 0$ . The linearized equations of motion are separated into two groups that correspond to modes of different symmetries I ( $\Delta M_z, \Delta m_z, \Delta L_y, \Delta l_y$ ) and II ( $\Delta M_y, \Delta m_y, \Delta L_z, \Delta l_z$ ), which are excited by the ac magnetic field  $\mathbf{h} \parallel \mathbf{c}$  ( $z$ ) and  $\mathbf{h} \parallel \mathbf{b}$  ( $y$ ), respectively. For oscillations of each symmetry, there are two resonance modes with the frequencies

$$\omega_{\pm}^2(\text{I, II}) = \frac{1}{2}B_{\text{I, II}} \pm \frac{1}{2}\sqrt{B_{\text{I, II}}^2 - 4C_{\text{I, II}}}, \quad (5)$$

where  $B_{\text{I, II}} = (\omega_{A6, A2} + \omega_{\text{R}}\eta)(\omega_{\text{E}} + \omega_{\text{R}}\eta) + 2\omega_{\text{R}}\omega_{\text{R}\parallel}\eta + \omega_{\text{R}}^2$ ,  $C_{\text{I, II}} = \omega_{\text{R}}\omega_{A6, A2}[\omega_{\text{E}, A2}\omega_{\text{R}} + \eta(\omega_{\text{E}}^2 - \omega_{\text{R}\parallel}^2)]$ ,  $\omega_{\text{E}} = \gamma_{\text{Fe}}(A + K_{A6}L_x^4)L_x/M_0$ ,  $\omega_{A2} = \gamma_{\text{Fe}}(K_{A2} + K_{A6}L_x^4)L_x/M_0$ ,  $\omega_{A6} = 6\gamma_{\text{Fe}}L_x^5K_{A6}/M_0$ ,  $\omega_{\text{R}, \text{R}\parallel} = \gamma L_x b_{\perp, \parallel}/\mu_{\text{B}} = 2L_x b_{\perp, \parallel}/\hbar$ ,  $\eta = \gamma_{\text{Fe}}m_0 l_x/\gamma M_0 L_x$ , and  $l_x = \tanh(L_x b_{\perp}/k_{\text{B}}T)$ . Each pair of frequencies  $\omega_{\pm}$  are the modes of the coupled spin oscillations of Fe and R ions, which are transformed, after the dilution of the R subsystem, to the eigenmodes of antiferromagnetic resonance Fe subsystem  $\sqrt{\omega_{A2, A6}\omega_{\text{E}}}$  and R modes, which are determined by the splitting of the doublet by the static exchange field  $\omega_{\text{R}} = 2L_x b_{\perp}/\hbar$ , respectively. The contributions from resonance modes I and II to the corresponding components of the high-frequency magnetic permeability are given by the expression

$$\Delta\mu_{\pm}(\text{I, II}) = \Delta\mu^{\text{Fe}} f_{\pm}^{\text{Fe}}(\text{I, II}) + \Delta\mu_{\parallel, \perp}^{\text{R}} f_{\pm}^{\text{R}}(\text{I, II}), \quad (6)$$

where

$$\begin{aligned} f_{\pm}^{\text{Fe}}(\text{I}) &= \{ \pm \omega_{A6}\omega_{\text{E}} \mp \alpha \omega_{\pm}^2 [(1 + \tilde{g}_{\parallel}\eta)^2 + 2\eta\tilde{g}_{\parallel}(\omega_{\text{R}\parallel}/\omega_{\text{R}} - 1)] \} / (\omega_{+}^2 - \omega_{-}^2), \\ f_{\pm}^{\text{R}}(\text{I}) &= [\pm(1 - \tilde{g}_{\parallel}^{-1})^2 \omega_{\text{R}}^2 \mp \alpha \omega_{\pm}^2] / (\omega_{+}^2 - \omega_{-}^2), \\ \alpha &= 1/[1 + \eta(\omega_{\text{R}}^2 - \omega_{\text{R}\parallel}^2)/\omega_{\text{E}}\omega_{\text{R}}] \approx 1 \end{aligned}$$

for modes I ( $\mathbf{h} \parallel \mathbf{c}$ ) and

$$f_{\pm}^{\text{Fe}}(\text{II}) = [\pm\omega_{A2}\omega_E \mp (1 + \tilde{g}_{\perp}\eta)^2\omega_{\mp}^2]/(\omega_{+}^2 - \omega_{-}^2),$$

$$f_{\pm}^{\text{R}}(\text{II}) = [\mp\omega_{\mp}^2 \pm (1 - \tilde{g}_{\perp}^{-1})^2\omega_{\text{R}}^2 \pm 2\tilde{g}_{\perp}^{-1}\omega_{\text{R}}(\omega_{\text{R}} - \omega_{\text{R}\parallel})]/(\omega_{+}^2 - \omega_{-}^2)$$

for modes II ( $\mathbf{h} \parallel \mathbf{b}$ ) and

$$\Delta\mu^{\text{Fe}} \equiv 4\pi\chi_{\perp} = 4\pi\gamma_{\text{Fe}}M_0L_x/\omega_E,$$

$$\Delta\mu_{\parallel,\perp}^{\text{R}} \equiv 4\pi\chi_{\parallel,\perp}^{\text{R}} = 4\pi\gamma m_0 l_x g_{\parallel,\perp}^2/4\omega_{\text{R}},$$

$$\tilde{g}_{\parallel,\perp} = \gamma g_{\parallel,\perp}/2\gamma_{\text{Fe}} = g_{\parallel,\perp}/g_{\text{Fe}}.$$

In the above analysis, we neglected the magnetoelectric interactions, which are also responsible for the excitation of modes in the electric field [14], because their contribution to the dielectric (magnetoelectric) susceptibility is small for the modes observed in the range under investigation. Using Eqs. (5) and (6), we analyzed and numerically simulated the observed resonance modes (see lines in Figs. 1, 2). Let us discuss particular iron borates in more detail.

**NdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> iron borate.** As can be seen in Fig. 1a, modes of the same symmetry have noticeably different frequencies; for this reason, their frequencies and contributions can be approximately ( $B^2 \ll 4C$ ) represented in the form

$$\omega_{+}^2 \equiv (\omega_{+}^{\text{Nd}})^2 \approx \omega_{\text{R}}^2 + \omega_E\omega_{\text{R}}\eta + 2\omega_{\text{R}}\omega_{\text{R}\parallel}\eta, \quad (7a)$$

$$\omega_{-}^2 \equiv (\omega_{-}^{\text{Fe}})^2 \approx \omega_E\omega_{A6}\omega_{\text{R}}^2/\omega_{+}^2,$$

$$\Delta\mu_{+} \equiv \Delta\mu_{+}^{\text{Nd}} \approx \Delta\mu_{\parallel}^{\text{R}}(1 - \tilde{g}_{\parallel}^{-1})^2\omega_{\text{R}}^2/\omega_{+}^2, \quad (7b)$$

$$\Delta\mu_{-} \equiv \Delta\mu_{-}^{\text{Fe}} \approx \Delta\mu^{\text{Fe}}(1 + \eta\tilde{g}_{\parallel})^2 + \Delta\mu_{\perp}^{\text{R}} - \Delta\mu_{+},$$

for mode I ( $\mathbf{h} \parallel \mathbf{c}$ ) and

$$\omega_{+}^2 \equiv (\omega_{+}^{\text{Nd}})^2 \approx \omega_{\text{R}}^2 + \omega_E\omega_{A2} + \omega_E\omega_{\text{R}}\eta + 2\omega_{\text{R}}\omega_{\text{R}\parallel}\eta, \quad (8a)$$

$$\omega_{-}^2 \equiv (\omega_{-}^{\text{Fe}})^2 \approx \omega_E[\omega_{A2} - \eta(\omega_{\text{R}\parallel}^2 - \omega_{\text{R}}^2)/\omega_{\text{R}}]\omega_{\text{R}}^2/\omega_{+}^2,$$

$$\Delta\mu_{+}^{\text{Nd}} \equiv \frac{1}{2}\Delta\mu_{+}$$

$$\approx \frac{1}{2}\Delta\mu_{\perp}^{\text{R}}(1 - \tilde{g}_{\perp}^{-1})^2\omega_{\text{R}}^2/\omega_{+}^2 + \frac{1}{2}\Delta\mu^{\text{Fe}}\omega_{A2}\omega_E/\omega_{+}^2, \quad (8b)$$

$$\Delta\mu_{-}^{\text{Fe}} \equiv \frac{1}{2}\Delta\mu_{-} \approx \frac{1}{2}\Delta\mu^{\text{Fe}}(1 + \eta\tilde{g}_{\perp})^2 + \frac{1}{2}\Delta\mu_{\perp}^{\text{R}} - \frac{1}{2}\Delta\mu_{+}$$

for mode II ( $\mathbf{h} \parallel \mathbf{b}$ ). Since the spins of Fe<sup>3+</sup> ions in a real crystal are oriented along all of the easy directions in the basal plane at  $H = 0$ , contributions (8b) should be averaged by multiplying by 1/2. The high-lying modes  $\omega_{+}$  can be considered as R modes whose frequencies are much higher than the static splitting of the doublet  $\omega_{\text{R}}$  due to the interaction with low-lying modes. The modes  $\omega_{-}$  can in turn be interpreted as the modes of

antiferromagnetic resonance renormalized by the interaction with high-lying R modes due to a factor of  $(\omega_{\text{R}}/\omega_{+})^2$  in Eqs. (7a) and (8a); this interaction is responsible for their noticeable softening. In addition, for the  $\omega_{-}^{\text{Fe}}$  mode II associated with the oscillations of the vector  $\mathbf{L}$  out of the basal plane, the anisotropy constant is renormalized,  $\omega_{A2} \rightarrow \omega_{A2} - \eta(\omega_{\text{R}\parallel}^2 - \omega_{\text{R}}^2)/\omega_{\text{R}}$ , due to the anisotropy of the R–Fe exchange ( $\omega_{\text{R}\parallel} \neq \omega_{\text{R}}$ ), which can be responsible for the spin reorientation in iron borates. The contributions from both R modes increase with a decrease in  $T$  proportionally to the difference between the populations of the doublet levels, which is determined by  $l_x(T)$ . On the contrary, the contribution of the  $\omega_{-}^{\text{Fe}}(\mathbf{h} \parallel \mathbf{b})$  mode decreases in good agreement with the experimental data (Fig. 1d). The simulation of the temperature dependences of the frequencies and contributions in the molecular field approximation yields a satisfactory agreement with the experimental data at  $\omega_E \approx 107 \text{ cm}^{-1}$ ,  $\omega_{A2} \approx 0.24 \text{ cm}^{-1}$ ,  $\omega_{\text{R}} \approx 8.7 \text{ cm}^{-1}$ ,  $\omega_{\text{R}\parallel} \approx 9.13 \text{ cm}^{-1}$ ,  $g_{\parallel} \approx -0.9$ , and  $g_{\perp} \approx -2.4$  in general correspondence with the optical and magnetic data for NdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> [15, 24] and the parameters of the Fe subsystem ( $\omega_{A2}$ ,  $\omega_E$ ) [14]. The quantity  $\omega_{A6} \approx 3 \times 10^{-4} \text{ cm}^{-1}$ , which determines the low-frequency mode of the antiferromagnetic resonance and weakly affects the high-frequency modes, was taken from the data for YFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> [13]. Note that, according to Eqs. (7b) and (8b), contributions from ( $\mathbf{h} \parallel \mathbf{c}$  and  $\mathbf{h} \parallel \mathbf{b}$ ) high-lying modes depend not only on the magnitudes of the components of the magnetic moment of the doublet, but on their signs. More precisely, these contributions are sensitive to the ratio of the  $g$  factors for the Nd<sup>3+</sup> doublet ( $g_{\perp,\parallel}$ ) and Fe<sup>3+</sup> ions ( $g_{\text{Fe}} \approx 2$ ) due to the mixed character of the corresponding spin oscillations. The negative signs of the resulting components of the  $g$  tensor ( $g_{\perp,\parallel}$ ) of the ground doublet of Nd<sup>3+</sup>, which made it possible to describe the observed contributions of the modes, reflect this circumstance, and indicate the possibility of the determination of the absolute values of the  $g$  tensor. Theoretical aspects of this problem and the methods for determining the absolute values of  $g$  tensors were discussed in recent work [25].

The dilution of the Nd subsystem in the Nd<sub>0.4</sub>Y<sub>0.6</sub>Fe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> compound leads to a noticeable decrease in the difference between the frequencies of Nd and Fe modes. This system is well described by the theory (Fig. 1b) with the following parameters close to the pure NdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> compound:  $\omega_E \approx 110 \text{ cm}^{-1}$ ,  $\omega_{A2} \approx 0.20 \text{ cm}^{-1}$ ,  $\omega_{\text{R}} \approx 8.2 \text{ cm}^{-1}$ ,  $\omega_{\text{R}\parallel} \approx 8.2 \text{ cm}^{-1}$ ,  $g_{\parallel} \approx -1.4$ , and  $g_{\perp} \approx -2.3$ . However, these parameters should be considered to be effective because this compound is in the structure phase  $P3_121$  and the local

crystal symmetry of R and Fe ions in the  $\text{Nd}_{0.4}\text{Y}_{0.6}\text{Fe}_3(\text{BO}_3)_4$  compound is lower.

In  $\text{SmFe}_3(\text{BO}_3)_4$  (Fig. 1c), the behaviors of the frequency and contribution of the mode observed in the  $\mathbf{h} \parallel \mathbf{c}$  polarization are similar to the respective behaviors for neodymium iron borate and are determined by Eqs. (7a) and (7b), respectively. Since the Landé factor of the  $\text{Sm}^{3+}$  ion is small ( $g_J = 2/7$ ) and makes almost no contribution to the magnetization [8], the observation of a fairly intense Sm mode  $\omega_+^{\text{Sm}}$  is obviously due to its excitation through the Fe subsystem,  $\Delta\mu_+^{\text{Sm}} \approx (4\pi N\mu_B^2 l_x/b_\perp)(\omega_R^2/\omega_+^2)$ . The picture for modes in the  $\mathbf{h} \parallel \mathbf{b}$  polarization is noticeably different; namely, the frequency of the  $\omega_-$  mode does not decrease as in  $\text{NdFe}_3(\text{BO}_3)_4$ , but increases and is noticeably higher than the eigenfrequency of the antiferromagnetic resonance of the Fe subsystem  $\sqrt{\omega_{A2}\omega_E}$ . This mode makes a noticeable contribution to the magnetic susceptibility  $\Delta\mu^-$  as compared to the high-frequency mode  $\omega_+$ . This behavior is due to the strong anisotropy of the exchange splitting of the ground state,  $\omega_R \gg \omega_{R\parallel}$ . Since the resonance frequencies  $\omega_+$  and  $\omega_-$  are close to each other, initial expression (5) rather than Eq. (8a) should be used and, taking into account that  $\omega_R \gg \omega_{R\parallel}$  and  $g_{\parallel,\perp} \ll 2$ , the contributions of modes II ( $\mathbf{h} \parallel \mathbf{b}$ ) can be estimated as  $\Delta\mu_\pm \approx \Delta\mu_\pm^{\text{Fe}}(\tilde{\omega}_{A2}\omega_E/\omega_\pm^2)|\omega_\pm^2 - \omega_R^2|/(\omega_+^2 - \omega_-^2)$ . It can be seen that  $\Delta\mu_+$  for the high-frequency mode  $\omega_+$  is small because it is close to  $\omega_R$ . The quantitative description of the frequencies and contributions for  $\text{SmFe}_3(\text{BO}_3)_4$  (Figs. 1c, 1f) is obtained with  $\omega_E \approx 114 \text{ cm}^{-1}$ ,  $\omega_{A2} \approx 0.22 \text{ cm}^{-1}$ ,  $\omega_R \approx 13.2 \text{ cm}^{-1}$ ,  $\omega_{R\parallel} \approx 1.3 \text{ cm}^{-1}$ ,  $g_{\parallel} \approx 0.3$ , and  $g_{\perp} \approx 0.3$ .

To analyze the resonance modes in  $\text{GdFe}_3(\text{BO}_3)_4$ , we used the same approach, but took into account that the ground state of the isotropic ion  $\text{Gd}^{3+}$  is the  $^8S_{7/2}$  multiplet with  $S_{\text{Gd}} = 7/2$ . The vectors  $\mathbf{m}_{\text{Gd}} = (\langle \mathbf{S}_1 \rangle + \langle \mathbf{S}_2 \rangle)/(2S_{\text{Gd}})$ ,  $\mathbf{l}_{\text{Gd}} = (\langle \mathbf{S}_1 \rangle - \langle \mathbf{S}_2 \rangle)/(2S_{\text{Gd}})$ , where  $\langle \mathbf{S}_{1,2} \rangle$  are the average spins in two Gd sublattices, are used as the order parameters. In the absence of the external magnetic field,  $\mathbf{m}_{\text{Gd}} = 0$  and  $\mathbf{l}_{\text{Gd}} = (l_x, 0, 0)$ , where  $l_x = B_S(L_x b_\perp/k_B T)$  is determined by the effective field of the Fe subsystem in the state  $\mathbf{L} = (L_x, 0, 0)$ , where  $B_S$  is the Brillouin function for  $S = 7/2$ . The equations of motion for  $\mathbf{m}_{\text{Gd}}$  and  $\mathbf{l}_{\text{Gd}}$  are similar to Eq. (4b), where  $m_0 = S_{\text{Gd}}g_{\text{Gd}}\mu_B N$ ,  $\gamma \rightarrow \gamma_{\text{Gd}} = g_{\text{Gd}}\mu_B/\hbar$ , and  $g_{\perp,\parallel} \rightarrow g_{\text{Gd}} \approx 2$  should be substituted. The frequencies and contributions are also determined by Eqs. (5) and (6), respectively. Taking into account that  $\gamma_{\text{Gd}} \approx \gamma_{\text{Fe}}$  ( $g_{\text{Gd}} \approx g_{\text{Fe}}$ ), we get an almost annulment (compensation) of the contributions of the high-frequency

(Gd) mode  $\omega_+$  for both polarizations,  $\Delta\mu_+ \approx \Delta\mu_\perp^{\text{R}}(1 - \gamma_{\text{Fe}}/\gamma_{\text{Gd}})^2\omega_R^2/\omega_+^2$ , which explains their absence in the transmission spectra of  $\text{GdFe}_3(\text{BO}_3)_4$ .<sup>1</sup> A similar situation occurs in the uniaxial state at  $T < T_R$ . However, weak Gd modes were observed in the Raman spectra of  $\text{GdFe}_3(\text{BO}_3)_4$  [10] at frequencies near  $18 \text{ cm}^{-1}$ . Using these results and data reported in [13] for the low-frequency mode of antiferromagnetic resonance ( $\mathbf{h} \parallel \mathbf{b}$ ), which is below the available range, we simulated the temperature dependences of all modes in both easy-plane and uniaxial states. These dependences are shown in Fig. 2a and generally well describe the experimental data at  $\omega_E \approx 124 \text{ cm}^{-1}$ ,  $\omega_{A2} \approx 0.21 \text{ cm}^{-1}$ ,  $\omega_R \approx 5.0 \text{ cm}^{-1}$ ,  $\omega_{R\parallel} \approx 5.2 \text{ cm}^{-1}$ , and  $\omega_{R\parallel} - \omega_R \approx 0.23 \text{ cm}^{-1}$ .

As was mentioned above, Gd modes in transmission spectra were detected in mixed compounds that contain not only Gd, but also anisotropic Nd ions, e.g., in  $\text{Gd}_{0.5}\text{Nd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  (Fig. 2b). According to an analysis and simulation of the system with two types of R ions (isotropic  $\text{Gd}^{3+}$  and anisotropic  $\text{Nd}^{3+}$ ) in the above approach, the appearance of these modes is due to the violation of the compensation in the contribution to  $\mu(\omega)$  for the high-frequency (Gd) mode, which occurs for the Gd and Fe subsystems with  $g_{\text{Gd}} \approx g_{\text{Fe}}$ . We obtained the parameters  $\omega_E \approx 113 \text{ cm}^{-1}$ ,  $\omega_{A2} \approx 0.25 \text{ cm}^{-1}$ ,  $\omega_{\text{Gd}} \approx 6.4 \text{ cm}^{-1}$ ,  $\omega_{\text{Gd}\parallel} \approx 6.7 \text{ cm}^{-1}$ ,  $\omega_{\text{Nd}} \approx \omega_{\text{Nd}\parallel} \approx 8.2 \text{ cm}^{-1}$ ,  $g_{\parallel} \approx -2.4$ , and  $g_{\perp} \approx -0.9$ . The determined splitting of the levels of  $\text{Gd}^{3+}$  ( $\sim 6.4 \text{ cm}^{-1}$ ), which corresponds to an exchange field of about  $69 \text{ kOe}$  and coincides with the data reported in [20], is noticeably lower than the frequency of the Gd modes due to the interaction between the modes.

We also studied iron borates  $\text{Gd}_{0.96}\text{Nd}_{0.04}\text{Fe}_3(\text{BO}_3)_4$  and  $\text{Gd}_{0.75}\text{Nd}_{0.25}\text{Fe}_3(\text{BO}_3)_4$  with a large Gd content. However, the Gd mode in them was not observed. This indicates the importance of having a sufficient amount of anisotropic  $\text{Nd}^{3+}$  ions for its observation. From the frequencies of Nd modes that coincide with the splitting of the main doublet of  $\text{Nd}^{3+}$  at low concentrations, this splitting was directly determined in both the easy-plane and uniaxial states ( $\omega_R \approx \omega_{R\parallel} = 8.2 \text{ cm}^{-1}$ ) using the fact that the spin reorientation holds in these compounds at  $\sim 6 \text{ K}$ .

#### 4. CONCLUSIONS

Submillimeter spectroscopic studies of rare-earth iron borates with R = Nd, Sm, and Gd have detected resonance magnetic excitations in exchange-interact-

<sup>1</sup> Note that a similar decrease in the intensity (contribution) of the exchange mode for ferromagnets occurs in the case of the closeness of the gyromagnetic ratios for their magnetic sublattices [26], which is a manifestation of the sensitivity of contributions to the ratio of the  $g$  factors of the ions of the magnetic sublattices that is mentioned in the case of Nd.

ing antiferromagnetic (Fe) and paramagnetic R subsystems and revealed characteristic features of their dynamics. We have found the existence of the strong interaction between spin oscillations of Fe and R ions that forms the spectrum of coupled excitations in dependence on the type of the R ion and the anisotropy of the exchange splitting of its ground state (doublet). Due to this dynamic coupling, splittings of the ground state of the R ion in a static exchange field, which is determined from optical data, noticeably differ from the frequencies of excitations observed in the R subsystem. However, with a decrease in the concentration of R ions, the frequencies of their excitations approach the corresponding exchange splittings. It has been shown that the contributions to the magnetic susceptibility from coupled modes strongly depend on the difference between the  $g$  factors of Fe and R ions; this dependence makes it possible to determine the sign of these factors. A relatively large intensity of exchange (Nd) modes observed in  $\text{NdFe}_3(\text{BO}_3)_4$  is explained by an increase in their contribution at  $g_{\perp, \parallel}^{\text{Nd}} < 0$ . At the same time, in  $\text{GdFe}_3(\text{BO}_3)_4$  with close  $g$  factors of Fe and Gd ions, the total dynamic magnetic moment is compensated and the exchange (Gd) mode is not observed. However, in the substituted compound  $\text{Gd}_{0.5}\text{Nd}_{0.5}\text{Fe}_3(\text{BO}_3)_4$  with anisotropic Nd ions, this compensation is violated and the Gd mode is manifested. In  $\text{SmFe}_3(\text{BO}_3)_4$ , where  $\text{Sm}^{3+}$  ions very weakly interact with the external magnetic field, their excitation occurs through the Fe subsystem. A detailed theoretical analysis of the dynamic properties of the system has explained and quantitatively described the observed effects and has determined the parameters of the main interactions. We have neglected the magnetoelectric contribution to the observed excitations, which is small in the wavelength range under investigation, but can be manifested at lower frequencies. This contribution will be considered elsewhere.

We are grateful to A.S. Prokhorov for discussion of this work and valuable comments. This work was supported by the Russian Foundation for Basic Research, project nos. 10-02-00846 and 09-02-01355, and the Ministry of Education and Science of the Russian Federation, project no. 16.518.11.7034.

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Translated by R. Tyapaev