MAGNETISM
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Antiferromagnetic Resonance and Magnetic Anisotropy in Single Crystals of the YFe$_3$(BO$_3$)$_4$–GdFe$_3$(BO$_3$)$_4$ System

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Abstract—The antiferromagnetic resonance in single crystals of the YFe$_3$(BO$_3$)$_4$–GdFe$_3$(BO$_3$)$_4$ system is studied in the frequency range 25–140 GHz and the temperature range 4.2–50.0 K. It is established that the YFe$_3$(BO$_3$)$_4$ crystal containing only the magnetic subsystem of Fe^{3+} ions is an antiferromagnet with an easy anisotropy plane. The temperature dependences of the gaps in the antiferromagnetic resonance spectra of GdFe$_3$(BO$_3$)$_4$ and Y$_x$Gd$_{1-x}$Fe$_3$(BO$_3$)$_4$ are used to calculate the contributions of the Fe^{3+} and Gd^{3+} subsystems to the magnetic anisotropy of these crystals. The contributions are found to be close in magnitude and have opposite signs. This leads to a relatively weak uniaxial anisotropy field in the crystals under investigation. Since the exchange interaction between the Gd^{3+} and Fe^{3+} ions magnetizes the magnetic subsystem of gadolinium, both subsystems start to contribute simultaneously at the Néel temperature of the iron subsystem.

1. INTRODUCTION

Ferroborates are rare-earth magnets with a structure of the mineral huntite and the general formula RFe$_3$(BO$_3$)$_4$ (where R^{3+} stands for a rare-earth ion), which have been recently attracting considerable interest. At room temperature, these crystals have space group R32 [1, 2]. The interest expressed in these materials derives primarily from their magnetic properties, which are determined by the effect of the rare-earth subsystem, as well as by their remarkable optical properties [3–5]. The magnetoelectrical properties revealed recently in gadolinium and neodymium ferroborates [6, 7] suggest that these crystals belong to multiferroics, a family whose investigation has recently become a topic of broad interest.

The gadolinium ferroborate GdFe$_3$(BO$_3$)$_4$ is thus far the best studied representative of this family. Studies of the antiferromagnetic resonance in this crystal [8] showed that at the Néel temperature $T_N = 38$ K, the Fe^{3+} subsystem characterized by the easy-plane anisotropy undergoes antiferromagnetic ordering. The exchange interaction between the Gd^{3+} ions is fairly weak, but this subsystem becomes ordered through exchange interaction with the iron ions. The competition between the contributions from the iron and gadolinium subsystems brings about spontaneous reorientation at a temperature of 10 K to the easy-axis state. Phase transitions between the easy-axis and easy-plane states are possible in a magnetic field too, and antiferromagnetic resonance was used to establish magnetic phase dia-

grams for a crystal magnetized along the axis and in the basal plane. These phase diagrams were confirmed by measurements of magnetostriction and electrical polarization [6], as well as by magnetic studies and measurements of the Mössbauer effect [9].

We report on a study of the resonance and magnetic anisotropy of crystals in the YFe$_3$(BO$_3$)$_4$–GdFe$_3$(BO$_3$)$_4$ system. This system is of particular interest because the magnetic properties of YFe$_3$(BO$_3$)$_4$ are determined only by the Fe^{3+} ions. This offers a possibility for studying the magnetic anisotropy, which is inherent in the iron subsystem, and separating the contributions from the magnetic subsystems to the anisotropy of the gadolinium ferroborate GdFe$_3$(BO$_3$)$_4$ and other crystals in the huntite group.

2. EXPERIMENTAL RESULTS

The YFe$_3$(BO$_3$)$_4$ single crystals up to $3 \times 3 \times 3$ mm in size were grown by the technology described in [10]. The crystals were oriented using the face shaped as a regular triangle, whose plane coincides with the basal plane. The resonance properties were measured with a computerized antiferromagnetic resonance spectrometer operating in a pulsed magnetic field [11].

The resonance properties of YFe$_3$(BO$_3$)$_4$ were probed at frequencies of 25–140 GHz in magnetic fields **H** ∥ **c** and **H** ⊥ **c**. When the field is oriented in the basal plane, one observes a practically gapless antiferromagnetic resonance branch with the frequency depending linearly on the field (Fig. 1). This depen-
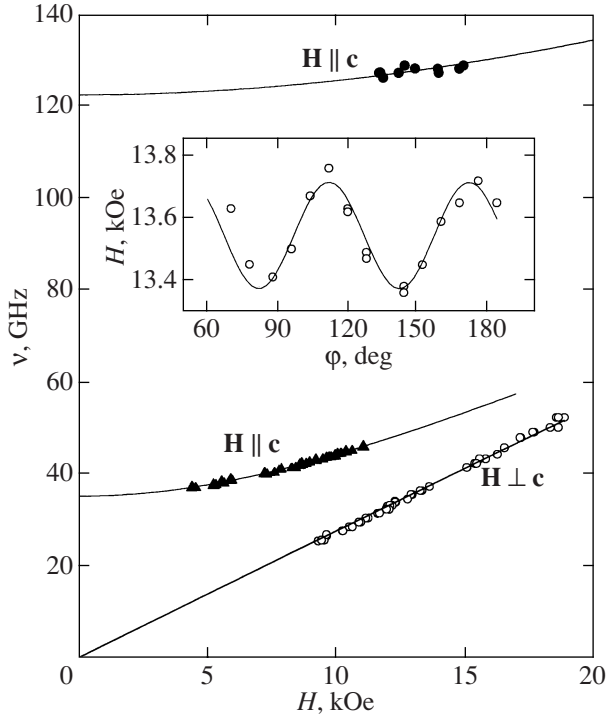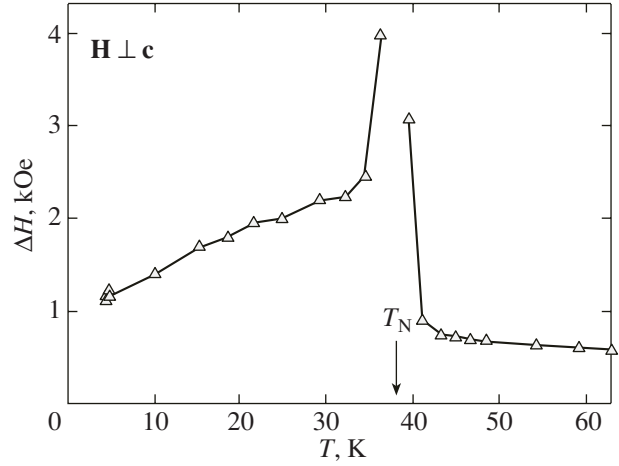
Fig. 1. Frequency–field dependences of the antiferromagnetic resonance in $YFe_3(BO_3)_4$ (circles) and $Y_xGd_{1-x}Fe_3(BO_3)_4$ (triangles). Open circles indicate the orientation $\mathbf{H} \perp \mathbf{c}$, and closed circles correspond to the orientation $\mathbf{H} \parallel \mathbf{c}$. The inset shows the angular dependence of the resonance field in the basal plane of $YFe_3(BO_3)_4$ at a frequency of 37.50 GHz. $T = 4.2$ K.

Fig. 2. Temperature dependence of the antiferromagnetic resonance line width for $YFe_3(BO_3)_4$ at a frequency of 36.75 GHz. $\mathbf{H} \perp \mathbf{c}$.

dence confirms the conclusion [8] that the iron subsystem is actually an antiferromagnet with an easy anisotropy plane, for which the oscillation frequencies can be written, if the weak anisotropy in the plane is taken into account, in the form [12]

$$\left(\frac{\omega_{\perp 1}}{\gamma_\perp}\right)^2 = H^2\left(1 + \frac{\left|H_A^{Fe}\right|}{2H_E}\right) + 2H_E H_{a6}\cos 6\varphi$$

$$\approx H^2 + 2H_E H_{a6}\cos 6\varphi, \qquad (1)$$

$$\left(\frac{\omega_{\perp 2}}{\gamma_\perp}\right)^2 = 2H_E\left|H_A^{Fe}\right| - \frac{\left|H_A^{Fe}\right|}{2H_E}H^2.$$

Here, $H_A^{Fe} < 0$ is the anisotropy field confining the magnetic moments to the basal plane and H_E is the exchange field. The low-frequency branch of $\omega_{\perp 1}$ is actually gapless, if we disregard the weak in-plane anisotropy. The equation for $\omega_{\perp 1}$ was written assuming also that $\left|H_A^{Fe}\right|/2H_E \ll 1$ (in our case, as this will be shown, $\left|H_A^{Fe}\right|/2H_E \sim 10^{-3}$). The gyromagnetic ratio $\gamma_\perp = 2.76$ GHz/kOe is determined by the g factor, which is close in magnitude to that of the Fe^{3+} ion. The second

oscillation branch for $\omega_{\perp 2}$ is not observed under field scanning in this orientation because of the weak field dependence of the frequency in the achievable field range.

The angular dependence of the resonance field in the basal plane measured at $T = 4.2$ K at 37.51 GHz is presented in the inset to Fig. 1. The solid line plots Eq. (1) with $2H_E H_{a6} = 4.6 \pm 0.4$ kOe^2.

For the $\mathbf{H} \perp \mathbf{c}$ orientation, the resonance field is practically independent of temperature because of the contribution of anisotropy in the basal plane being weak, and the linewidth grows monotonically under heating, to diverge rapidly in the range of the Néel temperature $T_N \approx 38$ K (Fig. 2).

When the magnetic field is oriented along the principal crystallographic axis, the antiferromagnetic resonance spectrum contains one line whose frequency vs. field dependence is also displayed in Fig. 1. This dependence follows closely the relation [12]

$$\left(\frac{\omega_\parallel}{\gamma_\parallel}\right)^2 = 2H_E\left|H_A^{Fe}\right| + H^2. \qquad (2)$$

The initial splitting of the spectrum is, however, considerably larger than that for the gadolinium ferroborate. The temperature dependence of the energy gap in the spectrum of $YFe_3(BO_3)_4$ is shown in Fig. 3. The second oscillation branch observed in this field orientation is the Goldstone branch with $\omega = 0$.

We studied also antiferromagnetic resonance in $Y_xGd_{1-x}Fe_3(BO_3)_4$ single crystals with $x \approx 0.5$ (for the yttrium content was taken that of the charge of which the single crystals were grown). As a result of the decrease in the contribution of the Gd^{3+} subsystem to magnetic anisotropy caused by the partial substitution by Y^{3+} ions, the magnetic structure of this crystal remains easy plane down to $T = 4.2$ K. Throughout the

temperature range in which magnetic order persists above 4.2 K, the antiferromagnetic resonance spectrum obtained for $\mathbf{H} \perp \mathbf{c}$ exhibits a gapless resonant oscillation branch with a linear frequency–field dependence, similar to the corresponding branch for the pure yttrium ferroborate. When magnetized along the principal crystallographic axis of $Y_xGd_{1-x}Fe_3(BO_3)_4$, one observes an oscillation branch with frequency vs. field dependence described by Eq. (2) and an energy gap substantially smaller than that in $YFe_3(BO_3)_4$ (Fig. 1). The temperature dependence of the gap for a substituted crystal is shown in Fig. 3, to be compared with the gap width temperature dependences for the $GdFe_3(BO_3)_4$ easy-axis and easy-plane states adopted from [8].

3. DISCUSSION

An analysis of exchange interactions in $GdFe_3(BO_3)_4$ revealed [8] that Fe^{3+} chains can couple both via the $B–O_3$ triangular complexes and via Gd^{3+} chains, because of the subsystems being exchange coupled. Note, that while interaction via the rare-earth subsystem provides a noticeable contribution, the magnetic states of the iron subsystem in $GdFe_3(BO_3)_4$ and $YFe_3(BO_3)_4$ may be different. Our measurements suggest that the Néel temperatures of the two crystals coincide, while measurements performed on polycrystals [13] show them to differ by less than 1 K, and this difference can be readily accounted for by the difference between the ionic radii of Gd^{3+} and Y^{3+}. This suggests that exchange interaction between the Fe^{3+} chains is realized primarily via the $B–O_3$ complexes. A similar conclusion is drawn in [14], a spectroscopic study of magnetic phase transitions in the mixed system $Gd_{1-x}Nd_xFe_3(BO_3)_4$. There are grounds to believe that the Fe^{3+} subsystems in both crystals, $GdFe_3(BO_3)_4$ and $YFe_3(BO_3)_4$, reside in very similar states. Therefore, using the exchange and anisotropy fields obtained for $YFe_3(BO_3)_4$ in separating the contributions of the magnetic subsystems to the anisotropy of $GdFe_3(BO_3)_4$ and other rare-earth ferroborates appears valid.

Accepting the energy gap at $T = 4.2$ K to be $\nu_{c\parallel} = 124$ GHz and the exchange field for the Fe^{3+} subsystem in $YFe_3(BO_3)_4$, $H_E^{Fe} = 700$ kOe (as derived from the perpendicular susceptibility at $T = 4.2$ K), the effective anisotropy field for the iron subsystem can be estimated as $H_A^{Fe} \approx -1.44$ kOe. In $GdFe_3(BO_3)_4$, the ground state gap (easy-axis anisotropy) at the same temperature is 29.4 GHz [8], building up to a total anisotropy $H_A^{total} \approx 0.08$ kOe. Thus, the contribution of Gd^{3+} ions to the anisotropy of this crystal at $T = 4.2$ K can be estimated as $H_A^{Gd} \approx 1.52$ kOe.
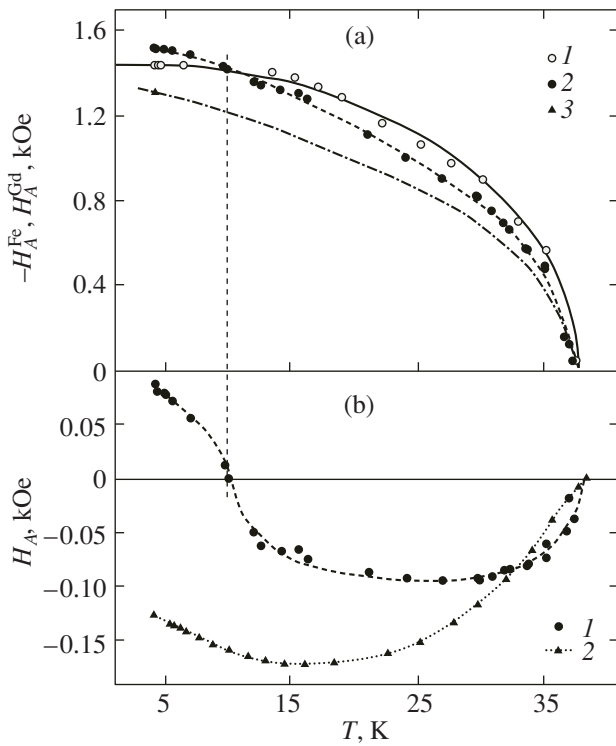
The temperature dependence of the anisotropy field for the iron subsystem can be derived from that of the
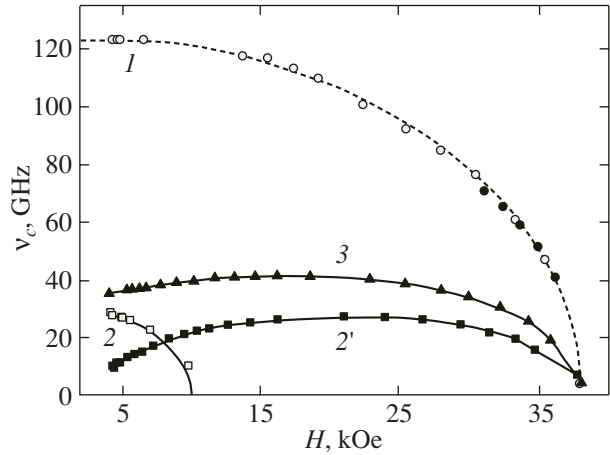
Fig. 3. Temperature dependences of the energy gap in the high-frequency antiferromagnetic resonance branches for crystals: (1) $YFe_3(BO_3)_4$ at frequencies of 127.88 GHz (open circles) and 78.77 GHz (closed circles), (2, 2') $GdFe_3(BO_3)_4$ in the (2) easy-axis and (2') easy-plane states [8], and (3) $Y_xGd_{1-x}Fe_3(BO_3)_4$. The dashed line indicates the Brillouin function for $S = 5/2$.

gap width in $YFe_3(BO_3)_4$. As follows from Fig. 3, the temperature dependence of the gap width can be fitted by the Brillouin function $B_{5/2}$ for the spin $S = 5/2$ normalized to the gap width at $T = 0$, which governs the temperature dependence of the relative sublattice magnetization $m(T)$. This suggests that the magnetic anisotropy of the iron subsystem in this crystal is driven by one of the pair mechanisms, namely, dipole–dipole interaction or exchange interaction anisotropy. In the case of a pair mechanism, the temperature dependence of the effective anisotropy field is proportional to $m(T)$, except for the low-temperature range, where the anisotropy field scales as $\sim m^2(T)$ [15]. And because within the molecular field theory the exchange field is also proportional to $m(T)$, in the most interesting temperature range where the sublattice magnetization varies in the most pronounced way the gap width scales as $\nu_{c2} = \gamma_\parallel \sqrt{2 H_E^{Fe} \left| H_a^{Fe} \right|} \sim m(T)$.

Figure 4a plots the temperature dependence of the absolute value of the iron subsystem anisotropy field H_A^{Fe} calculated from that of the gap width in $YFe_3(BO_3)_4$, with the scaling $H_E^{Fe} \sim m(T)$ included. Indeed, the temperature dependence of the anisotropy field is fitted well by the Brillouin function $B_{5/2}$ presented in the figure by a solid line. From the temperature dependences of the gap width for the easy-axis and easy-plane states of $GdFe_3(BO_3)_4$ (Fig. 3) one can derive the temperature dependence of the total anisotropy field; the results of the calculations are plotted in Fig. 4b. The latter relation was used to obtain, with due account of the contribution of the iron subsystem, the temperature dependence of the Gd^{3+} subsystem contri-

Fig. 4. (a) Temperature dependences of the anisotropy field of (*1*) the iron subsystem H_A^{Fe} and the contributions of the gadolinium subsystem H_A^{Gd} in (*2*) GdFe$_3$(BO$_3$)$_4$ and (*3*) Y$_x$Gd$_{1-x}$Fe$_3$(BO$_3$)$_4$. The solid line indicates the Brillouin function for $X = 5/2$. (b) Temperature dependences of the total anisotropy field for (*1*) GdFe$_3$(BO$_3$)$_4$ and (*2*) Y$_x$Gd$_{1-x}$Fe$_3$(BO$_3$)$_4$.

bution to the total anisotropy of GdFe$_3$(BO$_3$)$_4$, which is also plotted in Fig. 4a.

The contributions of the subsystems to the total anisotropy of the gadolinium ferroborate are close in absolute magnitude while differing in their dependence on temperature. This is why the magnetic structure of this crystal is extremely sensitive to such factors as temperature, magnetic field and substitutions by ions of different species in both subsystems, which change the ratio of contributions to the total anisotropy of GdFe$_3$(BO$_3$)$_4$. Also, as the temperature is lowered, the Gd^{3+} subsystem starts to contribute simultaneously with the onset of magnetic ordering in the iron subsystem; the reason for this lies in that the gadolinium subsystem is ordered through exchange interaction with Fe^{3+} ions. The first neutron diffraction studies of the magnetic structure of compounds of the huntite family performed on NdFe$_3$(BO$_3$)$_4$ [16] showed that antiferromagnetic ordering does indeed occur at the Néel temperature simultaneously in both magnetic subsystem.

Partial diamagnetic substitution of gadolinium by Y^{3+} ions in Y$_x$Gd$_{1-x}$Fe$_3$(BO$_3$)$_4$ brings about a decrease in the Gd^{3+} subsystem contribution to magnetic anisotropy. Recalling the above values of the exchange and anisotropy fields for the Fe^{3+} subsystem, we can estimate the contribution of Gd^{3+} ions to the total anisotropy of this crystal at $T = 4.2$ K as $H_A^{\text{Gd}} \approx 1.31$ kOe; this value is specified by a triangle in Fig. 4a. The decrease in the Gd^{3+} ion contribution was found to be smaller than this could be expected from the yttrium ion content in the relation, which was set in the charge. The real contribution of Y^{3+} ions in the single crystals turned out apparently to be lower and, as follows from our estimates, it does not exceed $x \approx 0.15$.

The temperature dependence of the gap width for Y$_x$Gd$_{1-x}$Fe$_3$(BO$_3$)$_4$ has an unusual pattern (Fig. 3); indeed, as the temperature increases, the gap width increases and starts to decrease only at temperatures above 15 K, to vanish subsequently as $T \longrightarrow T_N = 38$ K. The temperature dependence of the effective anisotropy field calculated from the energy gap behaves in a similar way (Fig. 4a).

It may be suggested that partial substitution of gadolinium by Y^{3+} ions brings about only a decrease in the contribution of the Gd^{3+} subsystem to magnetic anisotropy in absolute value, while the relative temperature dependence of this contribution persists. In Fig. 4a, this dependence normalized against the experimental value obtained at $T = 4.2$ K is depicted by the dash–dotted line. We readily see that because of the temperature dependences of the contributions due to the Gd–Y and iron subsystem being qualitatively different, the difference of their absolute values, which determines the total anisotropy in Y$_x$Gd$_{1-x}$Fe$_3$(BO$_3$)$_4$, does indeed pass through a maximum in the vicinity of $T \approx 15$–20 K and decreases as the temperature is lowered still further.

4. CONCLUSIONS

Thus, our studies of antiferromagnetic resonance in YFe$_3$(BO$_3$)$_4$ have provided support to the opinion that the Fe^{3+} subsystem in crystals with a huntite structure is an antiferromagnet with easy-plane anisotropy. The temperature dependence of the anisotropy field shows that the uniaxial anisotropy of the iron subsystem is governed by one of the pair mechanisms, namely, the dipole–dipole or anisotropic exchange interaction. Measurements of the temperature dependences of the gaps in the antiferromagnetic resonance spectrum has permitted from of the contributions from the Fe^{3+} and Gd^{3+} subsystems to the magnetic anisotropy of GdFe$_3$(BO$_3$)$_4$; these contributions are close in magnitude and have opposite signs, which brings about a relatively weak uniaxial anisotropy field in this crystal. The contribution from the separation the gadolinium subsystem to the anisotropy is induced simultaneously

with the onset of antiferromagnetic order in the iron subsystem at the Néel temperature as a result of exchange interaction between the Fe^{3+} and Gd^{3+} ions. The difference between the temperature dependences of the contributions from the subsystems gives rise to a spontaneous spin reorientation in $GdFe_3(BO_3)_4$ at $T = 10$ K and to a decrease in the anisotropy field in $Y_xGd_{1-x}Fe_3(BO_3)_4$ at low temperatures.

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