Anisotropic energy gap of low-frequency AFMR mode in Fe$_x$Ga$_{1-x}$BO$_3$ single crystals

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Abstract. Diamagnetically diluted iron-gallium borate Fe$_x$Ga$_{1-x}$BO$_3$ single crystals have been studied by Antiferromagnetic Resonance (AFMR) at 77 K in the frequency range of 17 to 25 GHz in magnetizing fields up to 10 kOe. Anisotropic energy gap of the low-frequency AFMR mode has been determined under the rotation of the magnetizing field in the basal plane of the crystals. The results show a reduction of the anisotropic energy gap with decreasing $x$.

1. Introduction

Iron borate FeBO$_3$ possesses an extraordinary set of physical characteristics: magnetic, resonance, magneto-acoustic, optical, magneto-optical, etc. [1-3]; therefore, it can serve as a model for studying the magnetic properties of condensed matter. FeBO$_3$ belongs to a very restricted family of magnetically ordered materials transparent for visible light [1]. This crystal is isostructural with CaCO$_3$: it has a rhombohedral calcite structure of $D_3^h$ space group possessing a three-fold axis $C_3$, three two-fold axes $C_2$ lying in the basal plane perpendicular to $C_3$, three symmetry planes $m$ perpendicular to $C_2$ and an inversion center [1]. From the viewpoint of magnetic structure, iron borate is a two-sublattice easy-plane antiferromagnet with the Néel temperature $T_N=348$ K, showing a weak ferromagnetism caused by the Dzyaloshinskii-Moriya interaction [1].

Various mechanisms determining the magnetic properties of FeBO$_3$ have different dependencies on iron contents and temperature. In order to provide a more detailed insight in magnetism of FeBO$_3$, we have recently proposed the approach of diamagnetic dilution – isomorphous substitution of a part of paramagnetic iron ions by diamagnetic ones [4]. In order to preserve the crystal structure of FeBO$_3$ in diluted crystals, the ionic radius of the diamagnetic ion should be close to that of Fe$^{3+}$, so, the evident choice is diamagnetic Ga$^{3+}$ [5]. We have synthesized a series of diamagnetically diluted iron-gallium borate, Fe$_x$Ga$_{1-x}$BO$_3$ single crystals with $x$ in the range of 0 to 1 by solution in the melt technique [4, 6-8]. The crystallizations have been carried out in Fe$_2$O$_3$-Ga$_2$O$_3$-B$_2$O$_3$-PbO-PbF$_2$ system, where B$_2$O$_3$, PbO, PbF$_2$ serve as solvents, Fe$_2$O$_3$, Ga$_2$O$_3$, B$_2$O$_3$ are crystal-forming reagents. Technological steps are as follows: preparing the charge, obtaining a homogeneous solution melt in a crucible, slow cooling of the solution melt in according to predetermined temperature mode and extracting of the synthesized crystals from the crucible. In order to obtain crystals with different $x$ different charge compositions and temperature modes have been used [4]. The synthesized samples
have the shape of thin hexagonal plates up to few millimeters in the basal plane and ca. 0.1 mm in the perpendicular direction. A high structural perfection of the crystals has been determined by high-resolution X-ray diffraction techniques [6, 9].

Studying the magnetic properties of diluted crystals, e.g., the magnetocrystalline anisotropy, allows specifying the nature of these magnetic characteristics of undiluted iron borate FeBO$_3$. The volume magnetocrystalline anisotropy of Fe$_x$Ga$_{1-x}$BO$_3$ has uniaxial and basal (hexagonal) components. The latter one is of interest in the present work and can be determined from studying the low-frequency (LF) mode of Antiferromagnetic Resonance (AFMR) [10].

Recently, we have studied Electron Magnetic Resonance (EMR) of Fe$_x$Ga$_{1-x}$BO$_3$ single crystals. Depending on iron contents and temperature, we have observed three distinct types of EMR in these crystals: (i) the LF AFMR, (ii) Cluster Magnetic Resonance (CMR) and (iii) Electron Paramagnetic Resonance (EPR) [11, 12]. With decreasing $x$, the EMR spectra show a gradual passage from AFMR at $x = 1$ towards the EPR of diluted iron ions at $x \ll 1$, going through a coexistence of AFMR and CMR arising, respectively, from magnetically ordered and partially disordered crystal regions for $0.34 \leq x \leq 0.85$, and CMR only for $x < 0.34$. A detailed study of LF AFMR mode has allowed us to determine the Dzyaloshinskii-Moriya field and isotropic energy gap for diluted crystals [12]. However, previously we have neglected a small anisotropic energy gap caused by basal anisotropy. The latter issue is the scope of the present work. We have studied Fe$_x$Ga$_{1-x}$BO$_3$ single crystals with relatively large Fe contents: 0.85 and 0.75, demonstrating relatively high $T_N$ in the range of ca. 280–320 K [13], interesting for practical applications [14]. The results for undiluted FeBO$_3$ have been published earlier [10].

2. Experimental details

The AFMR studies of Fe$_x$Ga$_{1-x}$BO$_3$ have been carried out at 77 K in the microwave frequency $\nu$ range of 17 to 25 GHz and magnetizing fields $H$ up to 10 kOe applied in the basal plane of the crystals. Figure 1 shows typical LF AFMR spectra at two different orientations of $H$. As one can see, the anisotropy of the resonance is observed in the basal plane of the crystals.

![Figure 1](image-url)
3. Results and discussion
For \( H \) applied in the basal plane of the crystal, the resonance frequency of the LF AFMR mode for \( \text{Fe}_{x}\text{Ga}_{1-x}\text{BO}_3 \) is given by the following expression representing a generalization of the one used in previous studies [10, 15]:

\[
\nu = \gamma \left[ H \left( H + H_D \right) + G_{\text{iso}} + G_{\text{aniso}} \right]^{1/2}
\]

where \( \gamma \) is the gyromagnetic ratio for the free-electron \( g \)-value, \( g \approx 2 \), \( H_D \) is the Dzyaloshinskii-Moriya field, \( G_{\text{iso}} \) and \( G_{\text{aniso}} \) are, respectively, the isotropic and anisotropic parts of the energy gap.

The angular dependencies of the total gap, \( G_{\text{tot}} = G_{\text{iso}} + G_{\text{aniso}} \), determined under the rotation of \( H \) in the basal plane of the crystals, are shown in Figure 2. It is seen that \( G_{\text{aniso}} \) contains a hexagonal contribution, \( G_{\text{hex}} \), caused by basal anisotropy, and a uniaxial contribution, \( G_{\text{ax}} \). The hexagonal contribution, congruent to the symmetry of the crystals, is described as [10]

\[
G_{\text{hex}} = G_{\text{hex}}^{\text{max}} \cos 6\phi \quad \text{where} \quad G_{\text{hex}}^{\text{max}} = 36H_E H_{\text{hex}}^{\text{max}},
\]

\( H_E \) is the exchange field, \( H_{\text{hex}} \) is the hexagonal anisotropy field and \( \phi \) is the angle between \( H \) and one of \( C_2 \) axes.

The uniaxial contribution can occur because of a slight deviation of \( H \) from the basal plane or mechanical stresses [16] and its angular dependence can be fitted to by the assuming a certain angular shift, \( f \), with respect to the hexagonal contribution:

\[
G_{\text{ax}} = G_{\text{ax}}^{\text{max}} \cos 2(\phi + f).
\]

The best-fit values of the parameters appearing in Equations (1 to 3) as well as previously determined \( H_D \) [12] for crystals with different \( x \) are listed in Table 1.

Table 1. The Dzyaloshinskii-Moriya field, the isotropic part of the energy gap, the amplitudes of the hexagonal and uniaxial contributions to the anisotropic part of the energy gap as well as the angular shift of the latter for \( \text{Fe}_{x}\text{Ga}_{1-x}\text{BO}_3 \) crystals with different \( x \).

| \( x \) | 1.0* | 0.85 | 0.75 |
|---|---|---|---|
| \( H_D \), kOe | 98.7±0.5 | 82.1±2.5 [11] | 74.10±0.25 [11] |
| \( G_{\text{iso}} \), kOe² | 6.55±0.05 | 3.06±0.06 | 3.83±0.42 |
| \( G_{\text{hex}}^{\text{max}} \), kOe² | 1.95±0.04 | 1.52±0.23 | 1.13±0.12 |
| \( G_{\text{ax}}^{\text{max}} \), kOe² | 1.13±0.05 | -0.53±0.08 | 0.68±0.03 |
| \( f \), deg | 0 | -4±4 | 19.5±1.3 |

* The data for \( x=1.0 \) have been earlier published by some of the present authors [10].

The results show a net reduction of \( G_{\text{hex}}^{\text{max}} \) with decreasing iron contents. This can be explained by the fact that both \( H_E \) and \( H_{\text{hex}} \) decrease because of the diamagnetic dilution. Indeed, both these quantities depend on the iron contents. Moreover, \( H_E \) is also determined by the number of nearest iron neighbours of a given iron ion that also decreases with the diamagnetic dilution [17]. In the case of \( H_{\text{hex}} \) one should take into account that the basal anisotropy in trigonal magnets with zero orbital...
moment, such as Fe$_x$Ga$_{1-x}$BO$_3$, includes two main contributions: (i) crystal field and (ii) dipole-dipole [10]. The first contribution linearly depends on the contents of paramagnetic ions in the crystals [18] while the second contribution can occur only for “extended dipoles”, having non-negligible size [10]. Calculations of $H_E$ and $H_{hex}$ for diluted crystals are in progress and will be published elsewhere.

Figure 2. Dependence of $G_{tot}$ on $\varphi$ at 77 K for diluted Fe$_x$Ga$_{1-x}$BO$_3$ single crystals with $x = 0.85$ (top) and 0.75 (bottom). The curves are fittings according the sum of the Equations (2) and (3).
4. Conclusions

We have determined the anisotropic energy gap of LF AFMR mode for iron-gallium borates Fe$_x$Ga$_{1-x}$BO$_3$ with relatively high $x$ values. The decrease of the hexagonal part of the anisotropic energy gap, $G_{hex}^{max} = 36H_{hex}$, with the increase of diamagnetic dilution is explained by the fact that both $H_{hex}$ and $H_{eff}$ depend on iron contents per se as well as on the number of iron ions in the vicinity of a given iron ion.

Acknowledgement

This work was partially supported by the Russian Foundation for Basic Research (RFBR) and the Ministry of Education, Science and Youth of the Republic of Crimea in the framework of scientific project grant no. 18-42-910008 “p_a” and by the RFBR in the framework of scientific project grant no. 18-32-00210 “mol_a” (synthesis of some experimental samples).

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