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Electron magnetic resonance of iron-gallium borate single crystals

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ABSTRACT

Electron magnetic resonance (EMR) studies of iron gallium borate, $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$, single crystals have been carried out in the frequency range ca. 8–38 GHz in magnetizing fields up to 10 kOe and the temperature range of 4–310 K. With decreasing x in the range of $0.34 \leq x \leq 1$, the EMR spectra show a gradual passage from a low frequency antiferromagnetic resonance (AFMR) mode at $x=1$ toward a coexistence of AFMR and cluster magnetic resonance arising, respectively, from completely and partially magnetically ordered crystal regions. Temperature and concentration dependences of magnetic characteristics of iron gallium borates, namely, the Néel temperature, the Dzyaloshinskii Moriya field, and the isotropic energy gap, have been determined by means of AFMR. In contrast to unmixed FeBO_3 , $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with $0.34 \leq x \leq 0.85$ show anomalous nonmonotonic temperature dependences of the Dzyaloshinskii Moriya field with a maximum well below the Néel temperature suggesting the occurrence of another magnetic transition in this temperature range.

I. INTRODUCTION

Mixed iron gallium borates, $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$, are isostructural crystals of rhombohedral calcite type structure with point group symmetry D_{3d} and space group D_{3d}^6 in the Schönflies notation.^{1–4} They possess a threefold axis C_3 , three twofold axes C_2 lying in the basal plane perpendicular to C_3 , three planes of symmetry perpendicular to C_2 , and an inversion center.³

From the standpoint of magnetic properties, unmixed iron borate FeBO_3 is a two sublattice easy plane antiferromagnet with the Néel temperature $T_N = 348$ K, showing a weak ferromagnetism with the resulting magnetization caused by the Dzyaloshinskii Moriya interaction.⁵ This material is a promising candidate for practical applications in various branches of experimental science and engineering. In particular, on the basis of iron borate magnetic memory elements possessing high density of recording, magnetoacoustic and magneto optical transducers and sensitive instruments for measuring pressures and ultraweak magnetic fields can be

created.⁵ Besides, iron borate can be used as an excellent monochromator for synchrotron Mössbauer spectroscopy.^{6–8}

The characteristics of magnetically ordered crystals, such as the Néel temperature, the Dzyaloshinskii Moriya field, etc., can be substantially modified under diamagnetic dilution, i.e., partial substitution of paramagnetic ions by diamagnetic ones.^{9–11} In this instance, in order to preserve the crystal structure, the ionic radius r_i of the diamagnetic ion should be chosen close to that of the substituted paramagnetic ion. In the case of trivalent iron, $r_i = 0.645$ Å in sixfold coordination, the evident choice is gallium, with $r_i = 0.62$ Å in the same coordination.¹² Previously, we have developed a solution in the melt route for synthesizing diamagnetically diluted $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ single crystals of high structural perfection. Details of the crystal synthesis have been published earlier.¹ A high structural perfection of the crystals has been attested using high resolution X ray techniques.^{8,13} The X ray topograms of mixed crystals have indicated the absence of growth steps and macroscopic structural defects, such as cracks

and dislocations. Besides, our electron paramagnetic resonance (EPR) studies have allowed estimating the distribution widths of atomic coordinates in these crystals as ca. 0.0005 Å.¹⁴

Mixed iron gallium borate crystals are of a great interest both for solid state physics and materials science because of the following reasons:

- (i) They allow monitoring the transformation of magnetic properties under the transition from magnetically ordered to paramagnetic state and fine tuning the magnetic characteristics for applications.
- (ii) Understanding the properties of magnetically diluted crystals, in particular, the magnetocrystalline anisotropy, allows specifying the nature of these properties in unmixed iron borate. Indeed, various mechanisms contributing in these properties are expected to vary in a different manner under diamagnetic dilution; therefore, studying $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with different x offers the possibility to recognize the contributions of mechanisms involved.

As far as we are mainly interested in magnetic properties of the crystals, as a key experimental technique, we have used the electron magnetic resonance (EMR). This generic term refers to any type of magnetic resonance involving the electronic system, i.e., EPR, antiferromagnetic resonance (AFMR), cluster magnetic resonance (CMR), etc. EMR allows identifying magnetic states occurring for different iron contents and at different temperatures. Some of the present authors have determined by EPR the spin

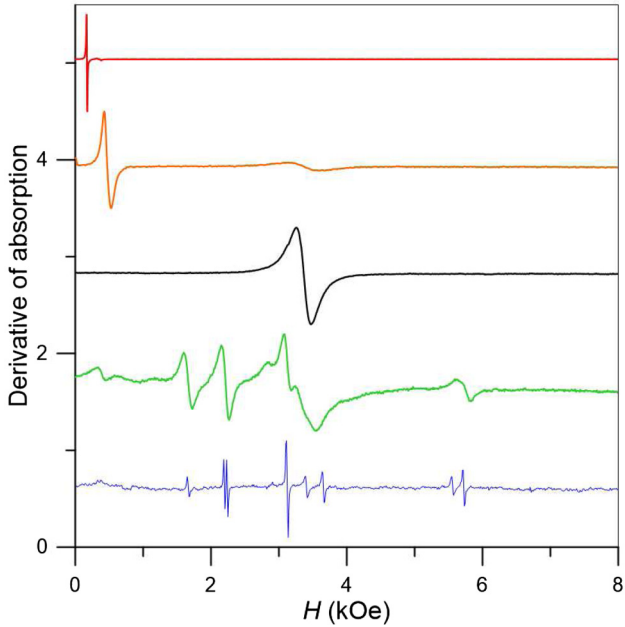


FIG. 1. Normalized X band room temperature EMR derivative of absorption spectra of $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with different x : 1 (a), 0.75 (b), 0.20 (c), 0.04 (d), and 0.003 (e).

Hamiltonian parameters of iron ions in $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with low x values¹⁴ and used them for theoretical analysis of certain magnetic characteristics, e.g., magnetocrystalline anisotropy in unmixed FeBO_3 .^{15,16} Besides, they have reported preliminary results of EMR studies of $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with higher x values.¹⁴ In this paper, we focus on the AFMR results for such crystals.

For a magnetizing field H applied in the basal plane of FeBO_3 , neglecting a small basal magnetocrystalline anisotropy,^{15,17} the low frequency (LF) AFMR mode is described by the following expression:^{18,19}

$$\nu = \gamma[H(H + H_D) + H_\Delta^2]^{\frac{1}{2}}, \quad (1)$$

where ν is the microwave frequency, γ is the gyromagnetic ratio for the free electron g value, H_D is the Dzyaloshinskii Moriya field, and H_Δ^2 is the isotropic energy gap, related to the resonance frequency in zero H and caused by elastic and magnetoelastic interactions.²⁰ Thus, using the AFMR, one can obtain both H_D and H_Δ^2 . Previously, using Eq. (1), these quantities have been obtained for unmixed FeBO_3 in a wide temperature range.¹⁸ As far as all crystals

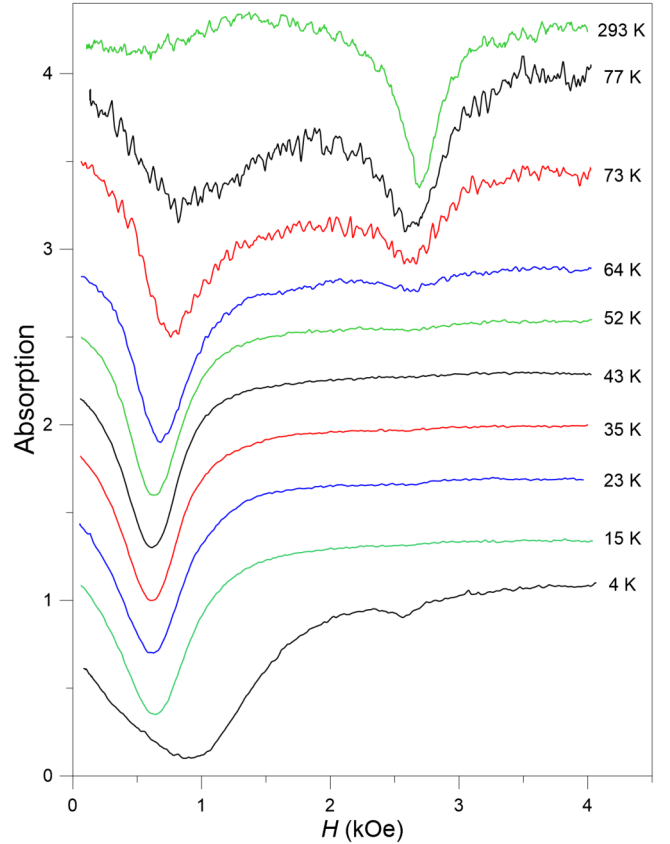


FIG. 2. Normalized EMR absorption spectra of $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystal with $x = 0.34$ at 7.67 GHz and different temperatures shown alongside the curves.

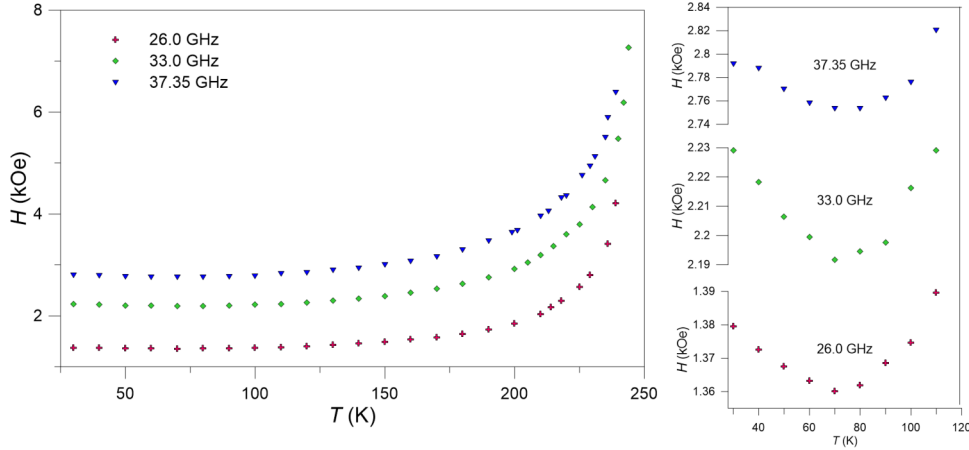


FIG. 3. Temperature dependences of the AFMR field for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystal with $x = 0.65$ measured at different frequencies (left) and their vertical zoom in the low temperature range (right).

in the $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ series are isostructural,^{1,2} this equation can be applied for such crystals as well.

In this work, using the AFMR technique, we have determined T_N , H_D , and H_Δ^2 for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with $0.34 \leq x \leq 0.85$.

II. EXPERIMENTAL RESULTS

The EMR studies of $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ single crystals have been carried out with two different field sweep spectrometers:

- (i) a laboratory developed transmission type spectrometer operating at a set of frequencies in the range ca. 8–38 GHz and recording “absorption” spectra,²¹ and
- (ii) a commercial high sensitivity X band (9.46 GHz) Bruker spectrometer recording “derivative of absorption” spectra.

In both cases, the crystals were studied in the temperature range of 4–310 K and magnetizing fields up to 10 kOe applied in the basal plane of the crystals.

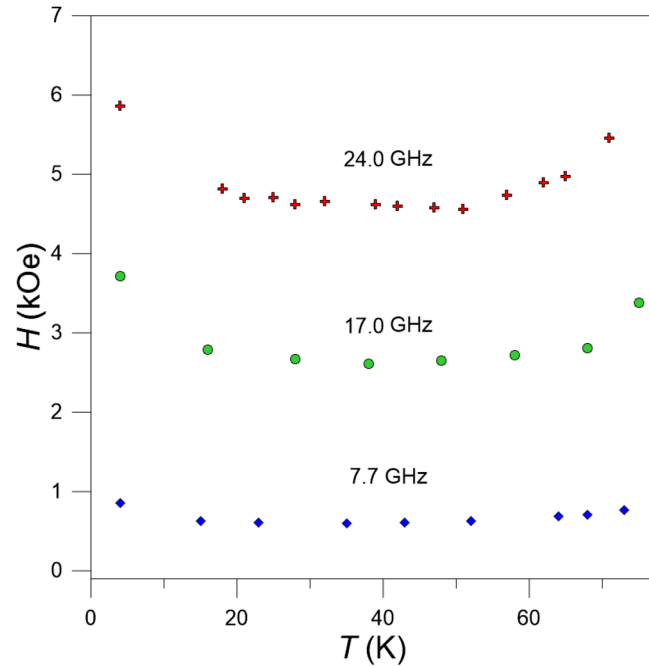


FIG. 4. Temperature dependences of the AFMR field for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystal with $x = 0.34$ measured at different microwave frequencies.

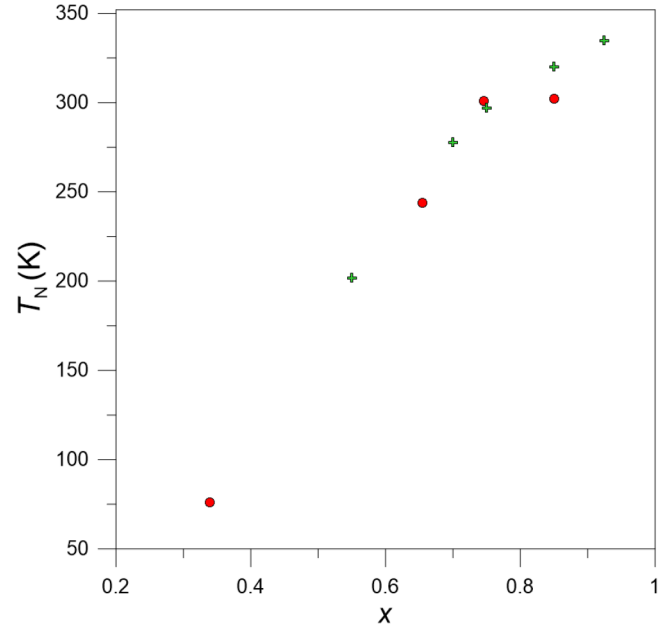


FIG. 5. Effective Néel temperatures for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with different x determined from AFMR measurements (filled circles, red online). Magnetometry and Mössbauer spectroscopy data²⁵ are included for comparison (crosses, green online).

Figure 1 shows the EMR spectra for crystals with different x . At $x=1$ (unmixed iron borate) only a low field resonance line is observed in the whole ranges of microwave frequencies and temperatures used in this work. This line has earlier been identified as LF AFMR.¹⁸ At a somewhat lower iron content, $x=0.75$, besides this low field line a new broad resonance line emerges in higher magnetic fields, with an effective g factor $g_{\text{eff}} = 2.0$. Assuming that iron substitution for gallium occurs more or less randomly, we can expect such crystals to contain regions with different local iron concentrations, implying different degree of magnetic ordering.

The low field line observed in mixed iron gallium borates can be reasonably identified by analogy with unmixed iron borate as the LF AFMR arising from completely magnetically ordered crystal regions. In turn, the high field line can be ascribed to CMR, i.e., EMR arising from only partially ordered regions, or, in the vicinity of the Néel temperature, to the superposition of CMR and EPR. At a still lower iron content, $x=0.2$, the AFMR line disappears and the high field line becomes more pronounced. For $x=0.04$, the latter line disappears as well, and the EPR spectrum of diluted Fe^{3+} ions broadened by dipole dipole interactions (Ref. 22 and references

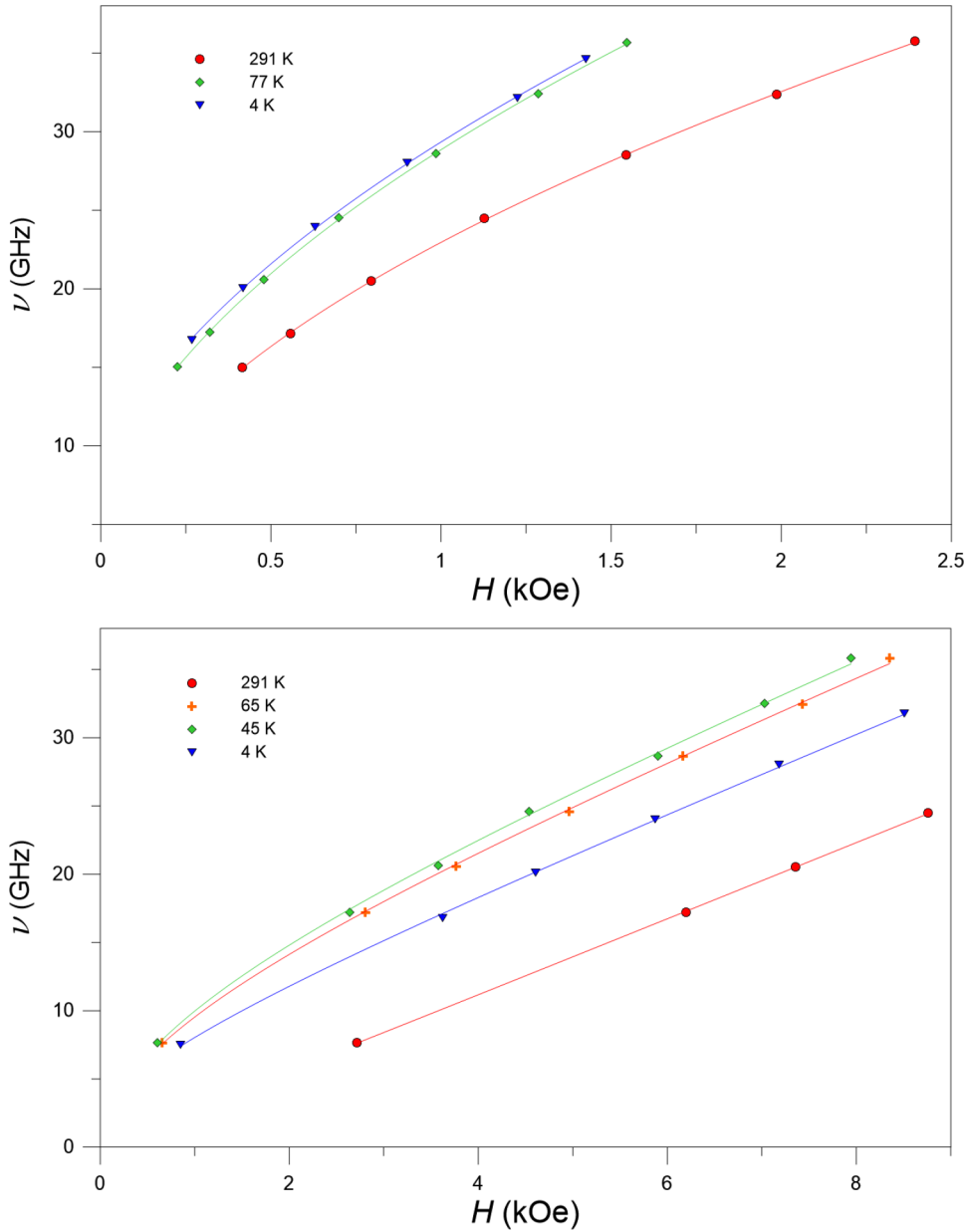


FIG. 6. FDRFs for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with $x=1$ (top) and 0.34 (bottom) at different temperatures. The solid curves are fittings according to Eq. (1).

quoted therein), comes into view. Finally, at a very lower iron content, $x = 0.003$, the latter spectrum is spectacularly narrowed.

Here, we focus on the AFMR results for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with iron contents in the range of $0.34 \leq x < 1$. Figure 2 shows the EMR spectra for $x = 0.34$ crystal at different temperatures. At room temperature only the high field line is present. At 77 K, a low field line emerges, indicating the onset of antiferromagnetic ordering so that this temperature can be considered as the Néel temperature for this crystal. In fact, in crystals with compositional disorder, a distribution of magnetic transition temperatures is expected²³ (in our case, the compositional disorder is caused by the random substitution of iron by gallium). Therefore, strictly speaking, this temperature should be considered as an “effective” Néel temperature. Obviously, the nature of the high field line observed at temperatures much higher than the latter one, e.g., at 293 K, can be only paramagnetic. With lowering the temperature from T_N , the AFMR line gradually shifts toward lower fields; simultaneously, its relative intensity increases. Similar spectra transformations in the vicinity of T_N occur in all crystals with $0.34 \leq x \leq 0.85$.

For $x = 0.34$ crystal, with lowering the temperature to ca. 20 K, see Fig. 2, the AFMR line slightly shifts downfield; meanwhile, a further cooling to 4 K results in a pronounced upfield shift and broadening of this line.

This behavior can be clearly seen in Figs. 3 and 4 showing the temperature dependences of the AFMR field (maximum of the resonance absorption) for crystals with $x = 0.65$ and 0.34 , respectively. In cooling the crystals down from T_N , the AFMR field first decreases, indicating a transition from paramagnetic to magnetically ordered state. Next, this decrease slows down, and below a certain temperature,

ca. 80 K for $x = 0.65$ and ca. 20 K for $x = 0.34$, the tendency is reversed, viz, the resonance shifts upfield. A similar behavior has been observed in all $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals studied in this work.

III. DISCUSSION

A. Néel temperature for mixed iron-gallium borates

Figure 5 illustrates the decrease of T_N with the decrease of x for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals, determined by AFMR. This behavior is quite naturally explained by the fact that in diamagnetically diluted crystals, the number of paramagnetic neighbors of a given paramagnetic ion is reduced so that the effective exchange field decreases.²⁴ For comparison, the data on T_N in similar crystals obtained by magnetometry and Mössbauer spectroscopy²⁵ are included. (In the original paper by Kamzin *et al.*,²⁵ they erroneously refer to their crystals as $\text{Fe}_{1-x}\text{Ga}_x\text{BO}_6$.) Obviously, the results of different determinations are in good agreement with each other.

B. Relationship between the antiferromagnetic resonance frequency and the magnetizing field

Figure 6 shows the frequency dependence of the resonance field (FDRF) for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with $x = 1$ and 0.34 at different temperatures. For $x = 1$ with decreasing the temperature, the FDRF monotonously shifts downfield, as earlier reported for unmixed FeBO_3 by Velikov *et al.*¹⁸ In contrast, for $x = 0.34$, it first shifts downfield and then upfield. In a greater or lesser extent, the latter compoment is characteristic of all mixed crystals with $0.34 \leq x \leq 0.85$.

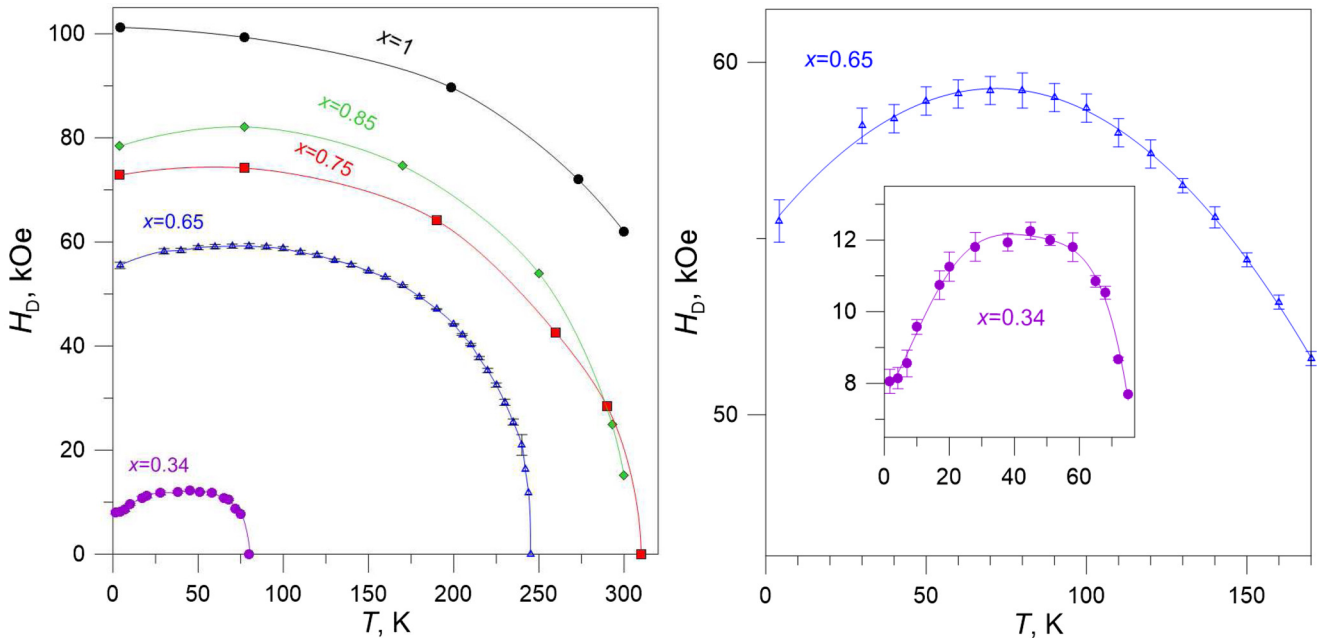


FIG. 7. Temperature dependences of the Dzyaloshinskii Moriya field in $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with different x (left) and a zoom in these dependences for crystals with $x = 0.65$ and $x = 0.34$ at low temperatures (right). The data for unmixed FeBO_3 ¹⁸ are included for comparison. The lines are guides for the eye.

By fitting the FDRFs with Eq. (1) using the least squares method, we have determined H_D and H_Δ^2 for different iron gallium borate crystals, *vide infra*.

1. Dzyaloshinskii-Moriya field

In cooling from T_N unmixed FeBO_3 , H_D shows a sharp increase in the temperature range ca. 350 to 80 K; at lower temperatures, this increase is slowed down, e.g., see Fig. 5(a) in the paper of Velikov *et al.*¹⁸ (and Fig. 7 in this paper). A quite different behavior is observed for mixed $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals (see Fig. 7). In cooling these crystals from T_N , H_D first increases and then passes through a maximum and finally decreases.

2. Isotropic energy gap

The data on H_Δ^2 for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with $0.34 \leq x \leq 1$ at different temperatures are shown in Table I. For comparison, bibliographic data for unmixed FeBO_3 are also included.

For crystal with $x = 0.34$, H_Δ^2 is very small, and, thus, it could be determined with reasonable accuracy only at $T = 4$ K. The crystals with higher iron contents have much larger low temperature H_Δ^2 values, comparable with those for unmixed FeBO_3 .

Detailed data on the temperature dependence of H_Δ^2 for $x = 0.65$ crystal are shown in Fig. 8. With decreasing the temperature from T_N to 4 K, H_Δ^2 increases. In the temperature range ca. 235 to 80 K, a sharp increase of H_Δ^2 is observed, while at lower temperatures this increase is slowed down. A similar behavior is observed for other crystals with intermediate iron contents as well as for unmixed FeBO_3 , e.g., see Fig. 6 in the paper by Velikov *et al.*¹⁸

C. The possibility of another magnetic transition below the Néel temperature

The transformations of the AFMR spectra and temperature dependences of the Dzyaloshinskii-Moriya field for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with different x , cf. Figs. 3, 4, 6, and 7, suggest that a certain change in the magnetic structure of these crystals occurs at temperatures well below T_N . Our SQUID measurements of the crystal with $x = 0.32$ show a reduction of the resulting magnetization below ca. 10 K (see Fig. 9). A possible explanation of this decrease is the reduction of the tilt angle between two sublattice magnetizations. This can occur if the antiferromagnetic vector (vector difference of the two sublattice magnetizations), initially lying in the basal plane, begins to rotate toward the C_3 axis. This

TABLE I. H_Δ^2 (in kOe^2) for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with $0.34 \leq x \leq 1$ at different temperatures.

T (K)	x				
	0.34	0.65	0.75	0.85	1.0 ¹⁸
4	0.75 ± 0.45	5.20 ± 0.45	6.02 ± 0.45	4.3 ± 0.5	4.9 ± 0.2
77	...	4.90 ± 0.30	5.00 ± 0.15	3.9 ± 1.2	4.25 ± 0.25
200		1.65 ± 0.10	0.7 ± 0.2		1.6 ± 0.2
250		0.70 ± 0.55	
300				...	0.6 ± 0.5

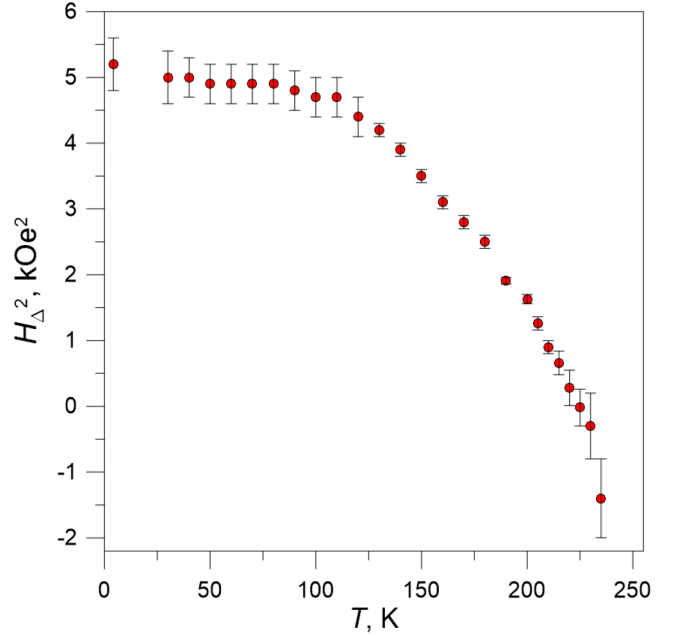


FIG. 8. Temperature dependence of the isotropic energy gap for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystal with $x = 0.65$.

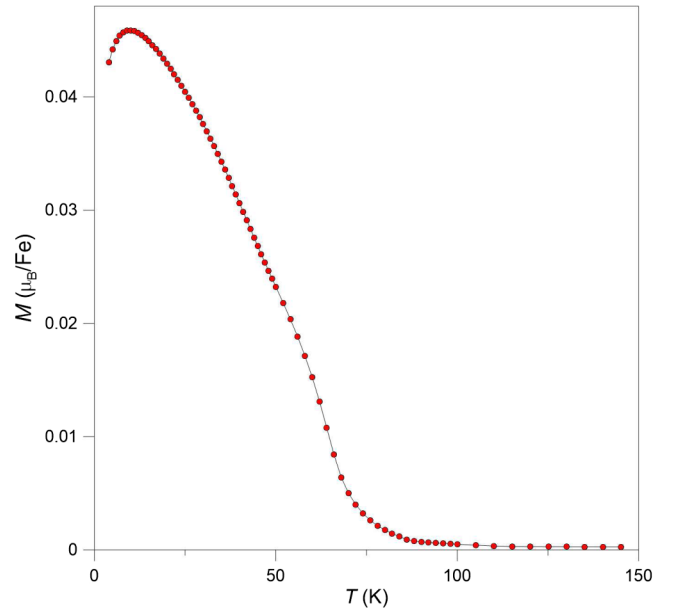


FIG. 9. Temperature dependence of resulting magnetization in the basal plane for $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystal with $x = 0.32$ measured in 100 Oe direct current magnetic field applied in the basal plane.

would initiate a transition from easy plane antiferromagnet with weak ferromagnetism to easy axis antiferromagnet, in which case weak ferromagnetism is absent. Such a transition, called the Morin transition, is known to arise in both undiluted and diamagnetically diluted hematite.^{26–29}

IV. CONCLUSIONS

In mixed iron gallium borates, $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$, we have observed three distinct types of EMR: (i) AFMR (LF mode), (ii) CMR, and (iii) EPR. With decreasing x , the EMR spectra show a gradual passage from AFMR at $x=1$ toward the EPR of diluted iron ions at $x \ll 1$, going through a coexistence of AFMR and CMR arising, respectively, from completely and partially magnetically ordered crystal regions for $0.34 \leq x \leq 0.85$, and CMR only for $x < 0.34$. Obviously, these crystals are of major interest for fundamental research.

The present study demonstrates the versatility of physical characteristics of mixed iron gallium borates. Indeed, the Néel temperature, the Dzyaloshinskii Moriya field, and the isotropic energy gap, determined by AFMR in this work, substantially decrease with decreasing x . Due to the possibility of predetermining their properties simply by varying their composition, these materials are extremely promising candidates for numerous technical applications.

$\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals with $0.34 \leq x \leq 0.85$ demonstrate an anomalous AFMR shift at low temperatures, which can be described in terms of decreasing the Dzyaloshinskii Moriya field and the resulting magnetization, confirmed by our SQUID measurements. In order to further elucidate the nature of this transformation, we consider the possibility of neutron diffraction and Mössbauer spectroscopic studies of mixed iron borate crystals.

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