Exchange energy in diamagnetically diluted iron borate-based crystals

K Seleznyova¹,², Yu Mogilenec¹, M Strugatsky¹, S Yagupov¹ and J Kliava²

¹ V.I. Vernadsky Crimean Federal University, Simferopol, Crimea
² LOMA, UMR 5798 Université de Bordeaux-CNRS, Talence, France

E-mail: kira_seleznyova@mail.ru

Abstract. The analytical relation between the microscopic $a_{\text{ex}}$ and macroscopic $E^\text{m}$ exchange constants for diluted iron-gallium borates has been obtained. A computer code implementing a calculation of the macroscopic exchange constant for diluted iron-gallium borates has been put forward. A diamagnetically diluted crystal lattice has been generated using Monte-Carlo technique. We have found that the absolute value of the macroscopic exchange constant for diluted iron-gallium borates decreases with decreasing $x$, following a parabolic law.

1. Introduction

Mixed iron-gallium borates, Fe$_x$Ga$_{1-x}$BO$_3$ are diamagnetically diluted crystals based on iron borate, FeBO$_3$ [1-3]. The latter is a two-sublattice easy-plane weak antiferromagnet possessing $D^{3d}_{1h}$ space group symmetry [4]. Fe$_x$Ga$_{1-x}$BO$_3$ crystals are of a great interest in solid-state magnetism, offering a possibility to study in detail the transformation of magnetic properties and states under diamagnetic dilution. A series of these crystals with $0 \leq x \leq 1$ has been synthesized by some of the present authors, see Figure 1 [1].

![Figure 1. Fe$_x$Ga$_{1-x}$BO$_3$ single crystals with x in the range of 1 (left) to 0 (right) synthesized by the solution in the melt technique.](image)

Recently, we have studied diluted Fe$_x$Ga$_{1-x}$BO$_3$ crystals with different $x$ by electron magnetic resonance, nuclear magnetic resonance, SQUID-magnetometry, optical and magnetooptical techniques, etc. [5-10]. Depending on iron contents and temperature, different magnetic states, namely, antiferromagnetic with weak ferromagnetism, cluster and paramagnetic have been identified and studied in detail [5, 9]. Such magnetic characteristics, as the Néel temperature and the Dzyaloshinski-Moriya field have been shown to decrease with the diamagnetic dilution [7, 8]. One of the main
interactions affecting the magnetic properties of iron-borate based crystals is the exchange coupling. The latter decreases with increasing the contents of a diamagnetic impurity, because in diamagnetically diluted crystals both the numbers of paramagnetic ions and their paramagnetic neighbours are reduced [11].

The aim of the present work is to put forward a description of the behaviour of the exchange energy with diamagnetic dilution in iron-gallium borates.

2. Relation between macro- and microscopic exchange constants for iron borate

The sublattice magnetizations of FeBO$_3$

$$\mathcal{M}_{1,2} = nm_{1,2}$$

(1)

with equal norms $\mathcal{M}$ ($\mathcal{M} = 520$ G at 0 K [4]) lie close to the basal plane and are nearly antiparallel-aligned [4]. In Equation (1), $m_{1,2}$ are magnetic moments of two Fe$^{2+}$ ions with equal norms $m$, belonging to different sublattices and $n = 1.118 \cdot 10^{28}$ m$^{-3}$ is iron concentration in one sublattice of FeBO$_3$ [4]. Because of a slight tilt between $\mathcal{M}_1$ and $\mathcal{M}_2$, ca. 55$^\circ$ [12], apart from a strong antiferromagnetic moment, $L = \mathcal{M}_1 - \mathcal{M}_2$ a weak ferromagnetic moment $M = \mathcal{M}_1 + \mathcal{M}_2$ occurs, and we can define reduced antiferromagnetic $l$ and ferromagnetic $m$ vectors:

$$l = \frac{1}{2} \frac{\mathcal{M}_1 - \mathcal{M}_2}{\mathcal{M}}$$

and

$$m = \frac{1}{2} \frac{\mathcal{M}_1 + \mathcal{M}_2}{\mathcal{M}}.$$  (2)

Note that

$$l^2 + m^2 = 1$$  (3)

Taking into account only the nearest iron neighbours, the density of the exchange energy for undiluted FeBO$_3$ can be expressed as

$$\xi_{ex} = -Zn a_{ex} m_1 \cdot m_2$$  (4)

where $Z$ is the number of nearest iron neighbours for each iron ion ($Z = 6$ for FeBO$_3$), $a_{ex} < 0$ is the microscopic exchange constant for a pair of neighbouring iron.

Equation (4) can be rewritten through the vectors $l$ and $m$, cf. Equations (1) and (2):

$$\xi_{ex} = -6 n a_{ex} \frac{\mathcal{M}^2}{n} \left( m^2 - l^2 \right).$$  (5)

Taking into account Equation (3), one gets:

$$\xi_{ex} = \frac{1}{2} E + \frac{1}{2} Em^2$$  (6)

where

$$E = -24 a_{ex} \frac{\mathcal{M}^2}{n}$$  (7)

is the macroscopic exchange constant. For undiluted FeBO$_3$ at 0 K, $E = 6.26 \cdot 10^8$ Jm$^{-3}$ [13]. Thus, $a_{ex}$ can be expressed through the known parameters for undiluted iron borate:

$$a_{ex} = -\frac{1}{4\xi} E \frac{n}{\mathcal{M}}$$  (8)
In what follows, we assume \( a_{\text{ex}} \) to be the same for diluted crystals, and we do not take into account the excitation of a magnetic system, so that the numerical results obtained below are valid at 0 K.

3. Macroscopic exchange constant for diluted iron-gallium borates

For diluted iron-gallium borates, the density of the exchange energy can be expressed as follows:

\[
\xi_{\text{ex}}^{\text{dil}} = -a_{\text{ex}} \sum_{i=1}^{n_{\text{dil}}} Z_i \mathbf{m}_i \cdot \mathbf{m}
\]

where \( n_{\text{dil}} \) is the number of iron ions in one sublattice of a diluted crystal of unit volume and \( Z_i \) is the number of nearest neighbours for the \( i \)th iron ion.

Equation (9) can be rewritten through the vectors \( \mathbf{l} \) and \( \mathbf{m} \), cf. Equations (1) and (2):

\[
\xi_{\text{ex}}^{\text{dil}} = -a_{\text{ex}} \frac{\mathbf{l} \cdot \mathbf{m}^2}{n_{\text{dil}}} \sum_{i=1}^{n_{\text{dil}}} Z_i,
\]

where \( \mathbf{l} = n_{\text{dil}} \mathbf{m} \) is the norm of the sublattice magnetization in diluted Fe\(_x\)Ga\(_{1-x}\)BO\(_3\) crystals. Taking into account Equation (3), one gets:

\[
\xi_{\text{ex}}^{\text{dil}} = -\frac{1}{4} E^{\text{dil}} + \frac{1}{2} E^{\text{dil}} m^2
\]

where

\[
E^{\text{dil}} = -4a_{\text{ex}} \frac{\mathbf{l} \cdot \mathbf{m}^2}{n_{\text{dil}}} \sum_{i=1}^{n_{\text{dil}}} Z_i
\]

is the macroscopic exchange constant for mixed iron-gallium borates.

In order to calculate \( E^{\text{dil}} \), we have put forward a computer code implementing the calculation based on Equation (12). Monte Carlo technique has been used to generate the diamagnetically diluted crystal lattice for a given \( x \) [14], the probabilities of iron or gallium occupying a given sites being \( x \) or \( 1-x \), respectively. Figure 2 shows the spatial distribution of gallium and iron ions in Fe\(_x\)Ga\(_{1-x}\)BO\(_3\) in a layer parallel to the basal plane.

![Figure 2](image_url)

Figure 2. Monte-Carlo simulations of a spatial distribution of iron ions in Fe\(_x\)Ga\(_{1-x}\)BO\(_3\) crystals with different \( x \) in a layer parallel to the basal plane. The circles and empty spaces are iron and gallium ions, respectively.
The computed dependence of $E^\text{dil}$ on $x$ is shown in Figure 3. As one can see, for mixed iron-gallium borates $E^\text{dil}$ decreases with decreasing $x$, following a parabolic law.

![Figure 3. Computed dependence of $E^\text{dil}$ on $x$ (circles). The dashed line is calculated using Equation (13), vide infra, with experimental parameters quoted in the text.](image)

This trend is predictable; indeed, introducing the mean $z$-value, $\bar{Z} = \frac{1}{n^\text{dil}} \sum_{i=1}^{n^\text{dil}} Z_i$ and taking into account that in the case of $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$ crystals, $\bar{Z} = 6x$ and $n^\text{dil} = nx$, Equation (12) reduces to:

$$E^\text{dil} = -24a_{\text{ex}} \frac{\Psi^2}{n} x^2. \quad (13)$$

This expression perfectly fits the dependence obtained by numerical calculation, see Figure 3.

4. Conclusions
The microscopic exchange constant $a_{\text{ex}}$ for a pair of iron neighbours has been calculated through the macroscopic exchange constant $E$ for undiluted iron borate FeBO$_3$. Assuming that $a_{\text{ex}}$ remains the same in diluted crystals, we have obtained an analytical expression for macroscopic exchange constant $E^\text{dil}$ for diluted iron-gallium borates $\text{Fe}_x\text{Ga}_{1-x}\text{BO}_3$. We have put forward a computer code modelling the diamagnetically diluted crystal lattice by Monte-Carlo technique and implementing a summation over the nearest neighbours of iron ions. As a result, we have obtained the dependence of $E^\text{dil}$ on iron contents $x$ that follows a parabolic law and justified this by analytical calculations.

Acknowledgement
This work was supported by the RFBR in the framework of scientific project Grant no. 18-32-00210 “mol_a”.
References

[1] Yagupov S, Strugatsky M, Selezyanova K, Maksimova E, Nauhatsky I, Yagupov V, Milyukova E and Kliava J 2015 Phys. A 121 179
[2] Selezyanova K, Strugatsky M, Yagupov S, Postivey N, Artemenko A and Kliava J 2014 Proc. Int. Conf. on Oxide Materials for Electronic Engineering (Lviv, Ukraine) p 205-206
[3] Yagupov S, Maksimova E, Nayhatsky I, Yagupov V, Milyukova E, Selezyova K and Strugatsky M 2014 Proc. Int. Conf. on Oxide Materials for Electronic Engineering (Lviv, Ukraine) p 207-208
[4] Diehl R, Jantz W, Nolang B I and Wettling W 1984 Current Topics in Materials Science ed E Kaldis (New-York: Elsevier) 11 241
[5] Selezyanova K, Strugatsky M, Yagupov S, Postivey N, Artemenko A and Kliava J 2014 Phys. Stat. Sol. B 251 1393-1400
[6] Selezyova K, Sergeev N, Olszewski M, Stepien P, Yagupov S, Strugatsky M and Kliava J 2015 Solid State Nucl. Magn. Reson. 70 38-42
[7] Yagupov S, Strugatsky M, Selezyova K, Mogilenec Yu, Drobosekov A, Kreines N and Kliava J 2016 Abstracts of EASTMAG (Krasnoyarsk, Russia) p 273
[8] Selezyova K 2016 Thesis LOMA, UMR 5798 Université de Bordeaux
[9] Kliava J, Rosa P, Selezyova K, Strugatsky M and Yagupov S 2018 IEEE International Magnetics Conference (INTERMAG 2018) (Singapore) DOI: 10.1109/INTMAG.2018.8508600
[10] Edelman I, Malakhovskii A, Sokolov A, Sukhachev A, Zabluda V, Yagupov S, Strugatsky M, Postivey N and Selezyova K 2012 Functional materials 19 163-166
[11] Bertrand D, Fert A R, Legrand S, Redoulès J P and Schmidt M C 1981 J. Phys. C: Solid State Phys. 14 1789-1797
[12] Petrov M, Smolensky G, Paugurt A, Kizaev S and Chizov M 1972 Solid state physics 14 109-113 (in Russian)
[13] Eibshütz M. and Lines M 1973 Phys. Rev. B 7 4907-4915
[14] Devroye L 1986 Non-Uniform Random Variate Generation (New York: Springer-Verlag)