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ON THE CHOICE OF SPIN HAMILTONIAN FOR Fe^{3+} IN $Fe_xGa_{1-x}BO_3$ SINGLE CRYSTALS

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Electron magnetic resonance (EMR) spectra of iron-gallium borates $Fe_xGa_{1-x}BO_3$, with x varying from 0 to 1, were measured with an X-band (9.5 GHz) spectrometer (Bruker) in the temperature range from 4 to 290 K and static magnetic fields B up to 1 T. Depending on the iron contents and the temperature, several types of EMR have been observed. At low x values, only the electron paramagnetic resonance (EPR) of diluted Fe^{3+} ions is present. X-band EPR spectra have been computer simulated on the basis of a "conventional" spin Hamiltonian with Zeeman and fine-structure terms. Good fits to the experimental spectra have been obtained for different orientations of B. The best-fit parameters are reported.

Keywords: synthesis, iron-gallium borates, electron paramagnetic resonance, computer simulations.

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INTRODUCTION

Mixed iron-gallium borates, $Fe_xGa_{1-x}BO_3$ are extraordinary materials, combining room-temperature magnetism at large concentration of Fe^{3+} ions and high transparency up to near ultraviolet spectral range. All these crystals are isostructural, possessing rhombohedral calcite structure with space group D_{3d}^6 [1]. Isomorphous substitution between gallium and iron allows one to deeper understand the transformation of their unusual optical and magneto-optical characteristics under the transition from paramagnetic to magnetically ordered state. On the other hand, it offers a possibility to fine-tune the properties of these crystals in the course of synthesis and thus create new materials suitable for various technical applications.

1. SYNTHESIS

We have developed the synthesis technique and have prepared series of high quality $Fe_xGa_{1-x}BO_3$ single crystals in the whole range of $0 < x < 1$ [2]. Crystallizations were carried out in the Ga_2O_3-Fe_2O_3-B_2O_3-PbO-PbF_2 system. Optimal component ratios in the charge and temperature modes were determined by differential thermal analysis [3].

The temperature mode used to obtain crystals includes the following steps: (i), heating the furnace; (ii), homogenization of the melt; (iii), sharp temperature drop; (iv), nucleation and crystal growth; (v) and (vi), cooling the furnace. The seed holder with synthesized crystals is extracted between (iv) and (v) steps.

The crystals have the shape of thin hexagonal plates.

2. EPR STUDIES

The crystals were studied by EPR with an X-band (9.5 GHz) spectrometer (Bruker) in the temperature range from 4 to 290 K and static magnetic fields B up to 1 T.

Figure 1 shows the EPR spectra for $Fe_{0.003}Ga_{0.997}BO_3$ at 4 K and different orientations of B (polar angle ϑ with respect to the C_3 axis and azimuthal angle φ with respect to the C_2 axis, see axes definition in ref. [1]). Because of small crystal size, the exact orientations have been determined through careful trial and error computer fitting. A large anisotropy of the resonance fields and a pronounced angular dependence of linewidths are observed for all orientations except in the basal plane.

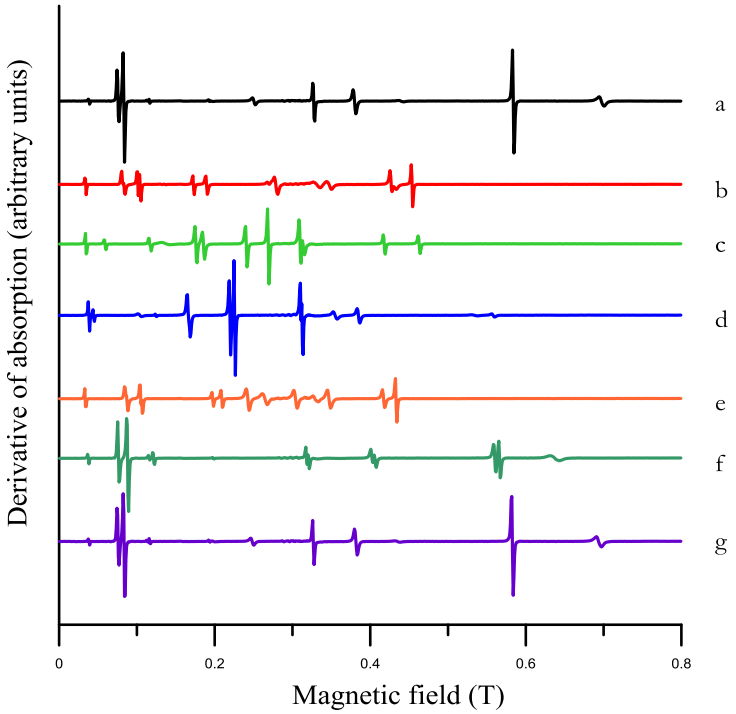

Fig. 1. EPR spectra for $Fe_{0.003}Ga_{0.997}BO_3$ crystal at 4 K for different orientations: a) $\vartheta = 11$, $\varphi = 0°$; b) $\vartheta = 37$, $\varphi = 30°$; c) $\vartheta = 66$, $\varphi = 37°$; d) $\vartheta = 96$, $\varphi = 41°$; e) $\vartheta = 135$, $\varphi = 48°$; f) $\vartheta = 164$, $\varphi = 69°$ and g) $\vartheta = 191.25$, $\varphi = 5.0°$.

The spectra intensities at different temperatures closely follow the $1/T$ Curie law. No temperature dependence of the spectra shape has been found.

Previously, the Fe^{3+} EPR in similar crystals has been studied by Lukin et al. at Q- (ca. 36 GHz) and V- (ca. 75 GHz) bands and accounted for in the frame of the "conventional" spin Hamiltonian of trigonal symmetry [4]:

$$\mathsf{H} = g\beta\mathbf{B}\cdot\mathbf{S} + \frac{1}{3}DO_2^0 - \frac{a-F}{180}O_4^0 + a\frac{\sqrt{2}}{9}\left(O_4^3 \cos 3\alpha \pm O_4^{-3} \sin 3\alpha\right) \qquad (4)$$

where all symbols have their usual meanings, O_2^0, O_4^0, O_4^3 and O_4^{-3} are extended Stevens operators, as defined in ref. [5, p. 512]. (Note that in refs. [4] and [5], instead of O_4^{-3}, notations $\widetilde{O}_4^{-3}$ and Ω_4^3 are used, respectively.) The $\pm$ signs in (4) refer to two magnetically non-equivalent Fe^{3+} ions in the crystal structure. For a nominal crystal composition with $x = 0.005$, Lukin et al. have obtained the following parameter values:

$D = 0.0989 \pm 0.0049$ (a more accurate value quoted in ref. [6]), $a = 0.0146$, F= -0.0052 (in cm^{-1}) and $\alpha = 24°$.

In order to check the validity of these results, we have carried out accurate computer simulations of our experimental X-band (9.464 GHz) EPR spectra for different orientations of B, using a laboratory-made code [7] based on eq. (4). In computer simulating the single crystal EPR spectra, the dependence of the intensities of various resonance lines on the orientation of microwave field (described by the azimuthal angle ψ with respect to the C_2 axis) has been taken into account, as well.

The best-fit parameters found:

$$D = 0.1032,\ a = 0.0158,\ F = -0.0052 \text{ (in cm}^{-1}\text{)} \text{ and } \alpha = 24°,$$

are in a reasonable agreement with those reported in [4].

Figure 2 demonstrates EPR spectra broadening with increasing the iron contents in the crystals.

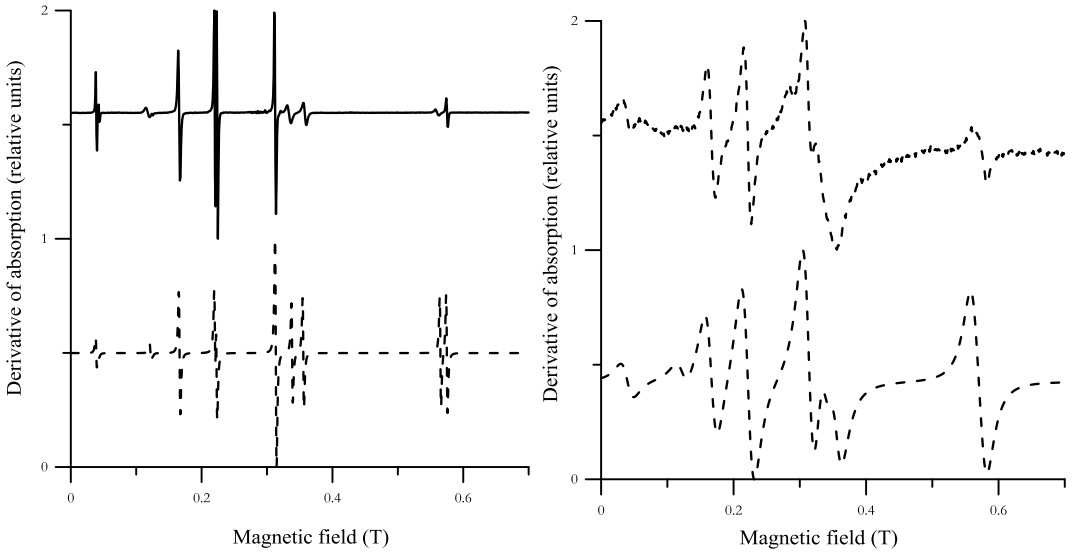

Fig. 2. Experimental room temperature (full lines) and computer generated (dashed lines) EPR spectra of $Fe_{0.003}Ga_{0.997}BO_3$ (left) and $Fe_{0.042}Ga_{0.958}BO_3$ (right). In both cases, $\vartheta = 87$, $\varphi = 15$ and $\psi = 60°$. The linewidth Δ_B, as deduced from the simulations, is 0.001 T for $Fe_{0.003}Ga_{0.997}BO_3$ and 0.0097 T for $Fe_{0.042}Ga_{0.958}BO_3$. All spectra are normalized to unity.

From Figure 2 one can see that the positions of different resonance lines are perfectly fitted to; however, relative amplitudes of certain lines are not quite satisfactorily reproduced in the simulations. Meanwhile, both the positions and intensities of all resonance lines have been calculated from eigenvalues and eigenvectors determined within the same diagonalization procedure of the spin Hamiltonian matrix. This discrepancy is related to a certain local disorder in the crystals resulting in statistical site-to-site distributions of the spin Hamiltonian parameters. As a consequence, for the lines with strong dependence of resonance fields on these parameters, pronounced broadening and concomitant amplitude decrease take place.

In order to provide a qualitative estimate of this effect, distributions of parameters *D, a* and *F* have been explicitly introduced in the simulation code. Besides, to account for disorder-induced lowering of the iron site symmetry, we have added to (4) a rhombic quadrupole fine-structure term EO_2^2 with zero mean *E*-value.

Taking into account the parameter distributions as well as the line intensity dependences on the angle ψ result in much better fits to the experimental EPR spectra, see Figure 3. Interestingly, in this case, good fits have been obtained without any distributions in *D*.

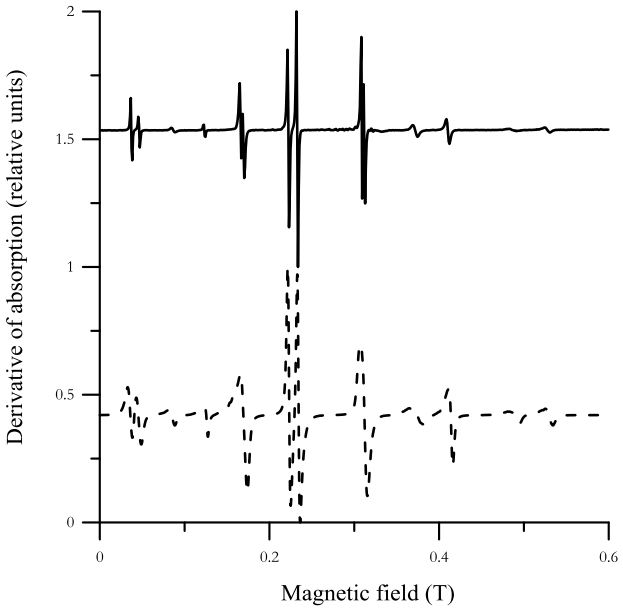

Fig. 3. Comparison between normalized experimental (full line) and computer generated (dashed line) EPR spectra taking into account parameter distributions: $\Delta_E = 0.005$, $\Delta a = 0.002$, $\Delta_F = 0.002$ (in cm^{-1}) for $Fe_{0.003}Ga_{0.997}BO_3$ ($\vartheta = 80.19$, $\varphi = 38.78$ and $\psi = 0°$). The mean parameter values are given in the text.

Finally, we have checked the consistency of the spin Hamiltonian parameter set quoted above, and we have found that exactly the same matrix of the spin Hamiltonian (4) could be obtained with the following parameter values:

$D = 0.1032$, $a = -0.0158$, $F = -0.0368$ cm^{-1} and $\alpha = 36°$.

To overcome this dichotomy, we have tested the compatibility of both parameter sets with the predictions of the Newman superposition model [8]. The corresponding results will be published elsewhere.

At higher x values, the characteristics of the EMR spectra of $Fe_xGa_{1-x}BO_3$ crystals become very complex, showing a gradual passage, first, from the EPR of diluted ions to the EMR of iron clusters and, next, to the antiferromagnetic resonance. The EMR studies of the corresponding phase transitions are in progress.

CONCLUSION

Electron magnetic resonance studies of $Fe_xGa_{1-x}BO_3$, with x varying from $0 < x < 1$ have demonstrated a gradual passage from the electron spin resonance of diluted Fe^{3+} to the antiferromagnetic resonance. Computer simulations of the Fe^{3+} spectra confirm previously reported results; however, they indicate a dichotomy in the spin Hamiltonian parameter definitions.

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Стругацький М. Б. Про вибір спінового Гамільтоніану для Fe^{3+} в монокристалах $Fe_xGa_{1-x}BO_3$ / М. Б. Стругацький, С. В. Ягупов, Н. С. Постивей, К. Селезньова, А. Артеменко, Я. Клява // Вчені записки Таврійського національного університету імені В. І. Вернадського. Серія : Фізико-математичні науки. – 2013. – Т. 26 (65), № 2. – С. 132-137.

Спектри електронного магнітного резонансу (ЕМР) залізо-галієвих боратів $Fe_xGa_{1-x}BO_3$ з x від 0 до 1 були виміряні Х-діапазонним (9.5 ГГц) спектрометром (Bruker) в температурному інтервалі від 4 до 290 К в статичних магнітних полях В до 1 Тл. Залежно від вмісту заліза і температури спостерігається кілька типів спектрів ЕМР. При низьких значеннях х має місце тільки електронний парамагнітний резонанс (ЕПР) розбавлених іонів Fe^{3+}. ЕПР спектри (Х-діапазон) були промодельовані за допомогою комп'ютера на основі «звичайного» спінового гамільтоніана з урахуванням зєємановського доданка і членів тонкої структури. Хорошу згоду з експериментальними спектрами було отримано для різних орієнтацій В. Найкращі значення параметрів наводяться.

Ключові слова: синтез, залізо-галієві борати, електронний парамагнітний резонанс, комп'ютерні модуляції.

Стругацкий М. Б. О выборе спинового Гамильтониана для Fe^{3+} в монокристаллах $Fe_xGa_{1-x}BO_3$ / М. Б. Стругацкий, С. В. Ягупов, Н. С. Постывей, К. Селезнева, А. Артеменко, Я. Клява // Ученые записки Таврического национального университета имени В. И. Вернадского. Серия : Физико-математические науки. – 2013. – Т. 26 (65), № 2. – С. 132-137.

Спектры электронного магнитного резонанса (ЕМР) железо-галиевых боратов $Fe_xGa_{1-x}BO_3$ с x от 0 до 1 были измерены X-диапазонным (9.5 ГГц) спектрометром (Bruker) в температурном интервале от 4 до 290 К в статических магнитных полях B до 1 Тл. В зависимости от содержания железа и температуры наблюдается несколько типов спектров ЕМР. При низких значениях x имеет место только электронный парамагнитный резонанс (ЕПР) разбавленных ионов Fe^{3+}. ЕПР спектры (X-диапазон) были промоделированы с помощью компьютера на основе «обычного» спинового Гамильтониана с учетом зеемановского слагаемого и членов тонкой структуры. Хорошее согласие с экспериментальными спектрами было получено для разных ориентаций B. Наилучшие значения параметров приводятся.

Ключевые слова: синтез, железо-галиевые бораты, электронный парамагнитный резонанс, компьютерные модуляции.

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