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The Magnetic Properties of GaFeO₃ by Neutron Diffraction and Mössbauer Spectroscopy

K. REĆKO^a, K. SZYMAŃSKI^a, L. DOBRZYŃSKI^{b,c} AND J. WALISZEWSKI^a^aFaculty of Physics, University of Białystok, Lipowa 41, 15-424 Białystok, Poland^bNational Centre for Nuclear Studies, A. Sołtana 7, 05-400 Otwock, Poland^cFaculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszyński University in Warsaw

K. Wóycickiego 1/3, 01-938 Warsaw, Poland

The multiferroic GaFeO₃ synthesized by a sol-gel method and conventional solid state reaction show remarkably different magnetic transition temperatures. Both samples have orthorhombic crystal structure *Pc2₁n*. Results of a new analysis of neutron diffraction and Mössbauer data are presented. Full agreement between parameters was achieved using the Mössbauer data as the constraints in the refinement of neutron diffraction data at low and at high temperature. Magnetic moments are reported.

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1. Introduction

Gallium iron oxide crystallizes in an orthorhombic crystal structure and its projection along [001] direction is shown in Fig. 1. The crystallographic unit cell contains 4 different cation sites and 6 oxygen anion sites all in general position (4a) of the *Pc2₁n* space group (no. 33). In the perfectly ordered structure sites labelled by Ga(1), Ga(2), and Fe(1), Fe(2) are entirely occupied by Ga³⁺ and by Fe³⁺ ions, respectively. The environment of gallium ion Ga(1) is almost a regular tetrahedron, while the other gallium and the two iron atoms are in distorted octahedral coordinations.

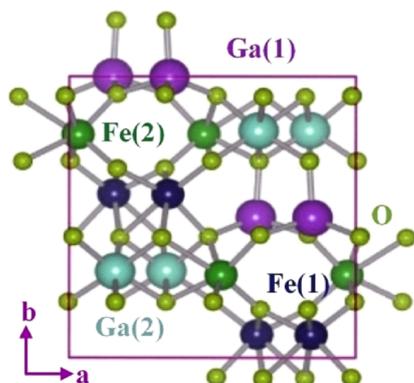


Fig. 1. The unit cell projection of the crystal structure of a perfectly ordered GaFeO₃ on basal plane.

Irrespectively of the GaFeO₃ synthesis method — single crystal flux growth [1], single crystal floating-zone melting [2–4], polycrystalline preparation by sol-gel (SG), or solid state reaction (SR) [5, 6] — the samples obtained show some cations' disorder, usually difficult for control. This is a problem because the physical properties of gallium ferrate are strongly dependent on the distribution of cations within the crystal structure

(see Table I). Moreover, the brief inspection of the data stored in Table I leads to the conclusion that the transition temperature seems to be closely related to the degree of order of the system.

The magnetic ground state of a perfectly ordered GaFeO₃ structure was determined by electronic structure calculations including spin-orbit interactions [7]. The system forms a collinear antiferromagnetic ordering along *c* direction with the calculated magnetic moment of irons equal to $\mu_{\text{Fe1}} = 4.27 \mu_{\text{B}}$ and $\mu_{\text{Fe2}} = -4.34 \mu_{\text{B}}$, respectively [7]. Any disorder among cations sites leads to ferrimagnetic [8, 9] or canted antiferromagnetic [10] structures. Recently it was demonstrated that two different methods of gallium ferrate preparation lead to the remarkably different Curie temperatures, T_{C} about 190 K for SR method and T_{C} above RT for SG method [5], see Table I. Origin of such large difference still remains unclear.

The influence of the crystalline grain size on the magnetic properties is not clear. The average size of the crystal grains prepared by solid state reaction was almost three times larger than that prepared by sol-gel method, i.e. ≈ 200 nm (SR) and ≈ 70 nm (SG). Moreover, it can be observed that the sample prepared by the sol-gel method gave a more homogeneous grain size distribution. According to X-ray measurements both of them were homogeneous. Moreover, to the Authors best knowledge the reduction of the particles size leads to [5]: (i) the reduction of stress in the lattice; (ii) the increase of the coercivity due to enhanced role of the surface and its anisotropy, and (iii) the enhancement of saturation magnetization attributed to surface spin-canting.

Three of the four cation's sites are equivalent by symmetry hence significantly impedes the quantitative analysis of the mixed (Fe/Ga) occupancy of the positions by diffraction methods. Aptly, the oxygen ligands form different coordinations around the central cations enhancing possibility of different site detection.

TABLE I

The review of the methods of GaFeO₃ preparation and phase transition temperatures with the selected structural parameters. The numerical data were taken from [1, 4, 5]. The stoichiometry of the samples were calculated from partial sites occupancies.

Sample stoichiometry	Method of preparation	Phase transition temperature	Site occupancy Fe/Ga	Lattice parameters at the lowest temperature
single crystal Ga _{0.93} Fe _{1.11} O ₃ [1]	flux method	300 K	Ga(1) — 14/86 Ga(2) — 32/68 Fe(1) — 83/17 Fe(2) — 89/11	$a \approx 8.725 \text{ \AA}$ $b \approx 9.374 \text{ \AA}$ $c \approx 5.066 \text{ \AA}$ (4 K)
single crystal Ga _{0.995} Fe _{1.005} O ₃ [4]	floating-zone method	< 230 K	Ga(1) — 10/90 Ga(2) — 24/76 Fe(1) — 84/16 Fe(2) — 83/17	$a = 8.71932(13) \text{ \AA}$ $b = 9.36838(15) \text{ \AA}$ $c = 5.06723(8) \text{ \AA}$ (4 K)
polycrystalline GaFeO ₃ [5]	solid state reaction	190 K	Ga(1) — 20/80 Ga(2) — 55/45 Fe(1) — 70/30 Fe(2) — 55/45	$a = 8.7327(6) \text{ \AA}$ $b = 9.3801(7) \text{ \AA}$ $c = 5.0743(9) \text{ \AA}$ (3 K)
polycrystalline Ga _{0.99} Fe _{1.01} O ₃ [5]	sol-gel	> 300 K	Ga(1) — 4/96 Ga(2) — 75/25 Fe(1) — 51/49 Fe(2) — 72/28	$a = 8.7478(7) \text{ \AA}$ $b = 9.4047(1) \text{ \AA}$ $c = 5.0793(9) \text{ \AA}$ (3 K)

The Mössbauer spectroscopy is sensitive to the local environment of iron. Since in GaFeO₃ different iron positions result in rather similar hyperfine parameters, the components of the Mössbauer spectra are strongly overlapped and difficult for unambiguous separation. Recently so-called method of invariants [11] was applied for simultaneous analysis of the Mössbauer spectra measured at high and at low temperature [6]. Although the method is dedicated to the systems with the same order of magnitude of the magnetic and quadrupole interactions, we have demonstrated that it can be successfully adopted for the samples with dominant magnetic interactions. The details of the method are given in [6] and are briefly outlined below. The line positions in the Mössbauer spectra are described by the invariants S_0 , S_1 , and S_2 , according to formulae (1)–(3):

$$S_0 = \varepsilon \sqrt{\text{Tr } \mathbf{V}^2}, \quad (1)$$

$$S_1 = \varepsilon \mathbf{m}^T \mathbf{V} \mathbf{m}, \quad (2)$$

$$S_2 = \varepsilon \sqrt{\mathbf{m}^T \mathbf{V}^2 \mathbf{m}}, \quad (3)$$

where \mathbf{V} is the tensor of the electric field gradient, and $\mathbf{m} = \mathbf{B}/B$, where \mathbf{B} is the hyperfine magnetic field pseudovector. The proportionality coefficient ε is a function of the elementary charge — e , the nuclear quadrupole moment — Q , the speed of light — c , and the energy between the ground and excited state — E_γ :

$$\varepsilon = eQc/E_\gamma. \quad (4)$$

Equation (5) illustrates the final relation which is proper for the systems of predominant magnetic interactions

$$2S_0^2 + 17S_1^2 - 20S_2^2 = 0. \quad (5)$$

In this paper we briefly present results of the analysis of the Mössbauer measurements and use some of them as the constraints in the analysis of the neutron diffraction data. The analysis allows to choose cations assignment to sites and to determine individual iron magnetic moments.

2. Experimental conditions and results

The Mössbauer spectra of the polycrystalline materials prepared by SR and SG methods [5] were collected in transmission geometry with a standard constant acceleration spectrometer and with the ⁵⁷Fe source in a Cr matrix. The appropriate components of the high and low temperature measurements were fitted simultaneously. Separation between the lines in high temperature (HT) spectra (not shown here) was proportional to the S_0 invariant, while line positions of low temperature (LT) spectra were constrained by S_1 invariant.

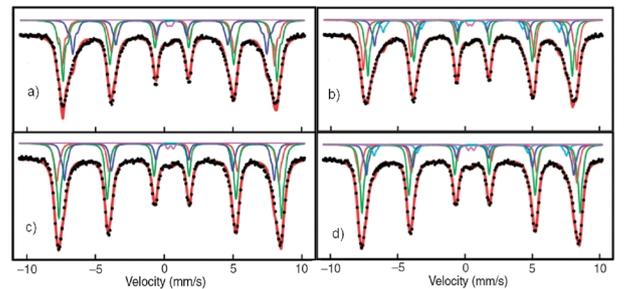


Fig. 2. Results of MS spectra fits of three (a) and four components (b) with the impurity phase for SR and of three (c) and four components (d) with the impurity phase for SG sample, respectively, recorded at $T = 14$ K.

TABLE II

Estimation of the sites occupancies of GaFeO₃ prepared by solid state reaction (SR) and sol-gel method (SG) based on relative areas of the Mössbauer spectra recorded at $T = 14$ K. Iron magnetic moments obtained are shown in the last line.

Site occupancy	SR Fe/Ga	SG Fe/Ga
Ga(1)	9/91(± 9)	8/92(± 9)
Ga(2)	42/58(± 6)	96/4(± 2)
Fe(1)	83/17(± 5)	45/55(± 4)
Fe(2)	66/34(± 3)	52/48(± 2)
$\mu_{\text{Fe_Total}}$	3.3(2) $\mu_{\text{B}}/\text{atom}$	4.1(3) $\mu_{\text{B}}/\text{atom}$

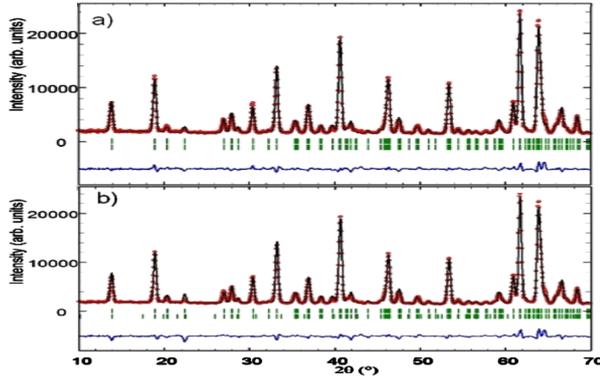


Fig. 3. Results of ND data refinements with the magnetic structure model of four (a) and three sublattices (b) for SG sample, measured at $T = 3$ K.

Both sites, Fe(1) and Fe(2), show strong disorder, especially in the case of SG preparation when iron sites ex-

hibit almost similar occupancy by Fe and Ga ions. Ga(2) sites in (SG) sample are occupied almost uniquely by Fe. Regardless of the method of preparation, the Fe concentration at Ga(1) site is very small (see Table II), thus the magnetic contribution of this position is not significant. Therefore, the analysis of MS spectra was carried out taking into account the three as well as four components, respectively (see Fig. 2a-d).

The most important result of the Mössbauer data analysis is that all iron atoms have very similar hyperfine fields and thus similar magnetic moments. Noteworthy, in the case of SR compounds fit (a) is visibly worse than (b) one, while for SG sample there are no significant differences between (c) and (d) fits.

The neutron diffraction measurements were carried out on diffractometer SPODI at FRM II (TUM, Germany) with the initial neutron beam of wavelength $\lambda = 1.5487$ Å at $T = 3$ K and RT. The structural properties were refined by the FullProf program package [12]. The iron occupancies of the cation's sites were taken from MS analysis and were supplemented by gallium while the anion sites occupancies were fixed during the whole refinement. The other crystallographic variables were free parameters.

The magnetic structure associated with the propagation vector $k = 0$ was determined after considering all irreducible representations permitted by the group theory for space group $Pc2_1n$. Let us remind that according to the notation of A , C , G , and F basic vectors of the irreducible representations for (4a) site the magnetic moments $m_{i=1\dots 4}$ of four Fe³⁺ ions can organize itself as follows: $A = m_1 - m_2 - m_3 + m_4$, $C = m_1 + m_2 - m_3 - m_4$, $G = m_1 - m_2 + m_3 - m_4$, and $F = m_1 + m_2 + m_3 + m_4$.

TABLE III

Sets of agreement factors [12] of the best refinements of ND patterns achieved for $\Gamma_1 = (A_x, C_y, G_z)$ with three and four magnetic sublattices, and with the appropriate magnetic moments expressed in [$\mu_{\text{B}}/\text{atom}$] determined at low- and high-temperature for different samples.

Site occupancy	SR_3 K Fe/Ga	SR_3 K Fe/Ga	SG_3 K Fe/Ga	SG_3 K Fe/Ga	SG_300 K Fe/Ga	SG_300 K Fe/Ga
Ga(1)	5/95(± 2)	0/100 fixed	12/88(± 6)	0/100 fixed	8/92	0/100 fixed
Ga(2)	45/55(± 2)	39/61	88/12(± 6)	78/22 fixed	96/4	78/22
Fe(1)	83/17(± 2)	90/10	43/57(± 3)	54/46 fixed	45/55	54/46
Fe(2)	67/33(± 2)	72/28	57/43(± 3)	69/31 fixed	52/48	69/31
(μ_x, μ_y, μ_z)	(0.35, 0.63, 3.13)	(0.30, 0.59, 3.32)	(0.45, 0.04, 4.03)	(0.40, 0.01, 3.63)	(0.57, 0.43, 1.75)	(0.44, 0.51, 1.62)
$\mu_{\text{Fe_Total}}$	3.21(7)	3.39(9)	4.06(8)	3.65(10)	1.89(11)	1.73(17)
\bar{R}_p	5.19	5.45	8.52	9.26	9.33	9.63
R_{wp}	6.22	6.51	9.46	9.16	9.97	10.41
R_{B}	1.82	2.30	3.77	7.02	4.07	4.46
R_{mag}	3.76	5.05	4.19	9.34	12.40	14.12

The best agreements between the experimental and calculated ND patterns were achieved for four magnetic sublattices (see 2nd, 4th and 6th columns of Table III). Similarly, Fig. 3a illustrates much better refinement of the low-angle part of the diagram than the lower one

shown in Fig. 3b. During the refinement of the HT data of systems with non-magnetic type of Ga(1) site the residual occupancies were treated as the free parameters (the uncertainties did not exceed 10%). Noteworthy, the ordering of cations and individual iron magnetic moments

depend strongly on the preparation conditions. An increase of on-site disordering systematically leads to lower magnetic moments of iron atoms, see Table III.

3. Conclusions

Definitely different chemical ordering on the cation's sites in GaFeO₃ is observed in systems synthesized according to SG and SR procedure. SG sample retains its ferrimagnetic character up to RT, while the temperature of the transition to paramagnetic state of SR is significantly lower. Magnetic moments of Fe³⁺ ions do not depend on their crystallographic positions in the system, but their spatial direction clearly changes with temperature. The analysis revealed that SG and SR prepared gallium ferrate exhibits a ferrimagnetic order with spins almost parallel to the *c*-axis. Moreover, the LT values of the total magnetic moments of Fe \approx 3.3 μ_B (SR) and \approx 4.1 μ_B (SG) are lower than predicted by theory [7].

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References

- [1] S. Mukherjee, A. Garg, R. Gupta, *J. Phys., Condens. Matter* **23**, 445403 (2011).
- [2] J.P. Remeika, *J. Appl. Phys.* **31**, 263S (1960).
- [3] S.C. Abrahams, J.M. Reddy, J.L. Bernstein, *J. Chem. Phys.* **42**, 3957 (1965).
- [4] T. Arima, D. Higashiyama, Y. Kaneko, J.P. He, T. Goto, S. Miyasaka, T. Kimura, K. Oikawa, T. Kamiyama, R. Kumai, Y. Tokura, *Phys. Rev. B* **70**, 064426 (2004).
- [5] M.B. Mohamed, A. Senyshyn, H. Ehrenberg, H. Fuess, *J. Alloys Comp.* **492**, L20 (2010).
- [6] K. Szymański, L. Dobrzyński, M.B. Mohamed, D. Satuła, W. Olszewski, G. Parzych, H. Fuess, *Phase Transit.* **83**, 824 (2010).
- [7] M.J. Han, T. Ozaki, J. Yu, *Phys. Rev. B* **75**, 060404 (2007).
- [8] R.B. Frankel, N.A. Blum, S. Foner, A.J. Freeman, M. Schieber, *Phys. Rev. Lett.* **15**, 958 (1965).
- [9] T. Arima, *J. Phys., Condens. Matter* **20**, 434211 (2008).
- [10] G.T. Rado, *Phys. Rev. Lett.* **13**, 335 (1964).
- [11] D. Satuła, K. Szymański, L. Dobrzyński, V.H. Tran, R. Troć, *Phys. Rev. B* **78**, 014411 (2008).
- [12] J. Rodríguez-Carvajal, *Physica B* **192**, 55 (1993).