Observation of multiferroicity in GaFeO₃ by Mössbauer spectroscopy

S Nakamura¹,², Y Kobayashi³, S Kitao³, M Seto³ and A Fuwa⁴

¹ Department of Science and Engineering, Teikyo University, Utsunomiya, Tochigi 320-8551, Japan
² Advanced Research Center of Science and Engineering, Waseda University, Shinjuku, Tokyo 169-8555, Japan
³ Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-0494, Japan
⁴ Faculty of Science and Engineering, Waseda University, Shinjuku, Tokyo 169-8555, Japan

E-mail: shin@koala.mse.teikyo-u.ac.jp

Abstract. The multiferroic nature of GaFeO₃ has been examined by ⁵⁷Fe Mössbauer spectroscopy in applied magnetic field. The spectra were analyzed as superposition of three subspectra corresponding to Fe³⁺ ions on Fe₁, Fe₂, and Ga₂ sites. The quadrupole coupling constants e²Q/2 are about twice of the calculated values, which may be partially due to the spin-orbit interaction. At 4.2 K, e²Q/2 of Fe₁ and Fe₂ sites increase noticeably when the magnetic field is applied along the c-axis. This is suggestive of the displacement of Fe ions toward -b direction. On the other hand, the increase of e²Q/2 is not observed when the magnetic field is applied along the b-axis. These features seem to be related to the toroidal moment. An increase of hyperfine field of Fe₁ site is observed when the magnetic field is applied. This may be also related to spin-orbit interaction.

1. Introduction

Gallium iron oxide GaFeO₃ has been known as both piezoelectric and ferrimagnetic [1]. It has an orthorhombic structure (Pc₂₁n) with lattice constants of a = 8.7442 Å, b = 9.3927 Å, and c = 5.0823 Å at room temperature. The crystal structure is shown in figure 1. The structure contains three octahedral cation sites (termed Fe₁, Fe₂, and Ga₂ sites) and one tetrahedral cation site (termed Ga₁ site). Both Fe³⁺ and Ga³⁺ ions occupy the three octahedral sites. The occupancies of Fe³⁺ ions are 0.77, 0.70, and 0.35 for Fe₁, Fe₂, and Ga₂ sites, respectively [2]. Fe³⁺ ions on Fe₁ and Fe₂ sites are located at non-center positions of the oxygen octahedrons with the displacements of +0.26 and -0.11 Å along the b-axis. As a result, the electric dipole appears along the b-axis. At the same time, the material is a ferrimagnet with the Curie temperature of about 200 K. The spins of Fe³⁺ on Fe₂ site and those on Ga₂ site form up-moments, whereas those on Fe₁ site form down-moments [3]. The magnetic easy direction is the c-axis. At low temperature, application of a magnetic field along the c-axis induces a
linear magnetoelastic (ME) effect with the electric dipole along the $b$-axis [2, 4]. This feature is explained by a toroidal moment, $T = r \times M$, where $r$ and $M$ represent the displacement of the Fe ion from the center of oxygen octahedron and the magnetic moment of the Fe ion, respectively. As mentioned above, the vectors $r$ are in +$b$ and −$b$ directions for Fe1 and Fe2 sites, respectively, while $M$ are in −$c$ and +$c$ directions for Fe1 and Fe2 sites, respectively. Therefore the modulation of the displacements at Fe1 and Fe2 sites are cooperative (i.e., toward −$b$ direction) when the magnetic field is applied along the $c$-axis, which produces a dielectric moment along −$b$ direction. On the other hand, they tend to cancel out when the magnetic field is applied along the $b$-axis [2, 4].

In order to clarify the origin of the ME effect, $^{57}$Fe Mössbauer spectroscopy is a useful probe having an observation time of 10$^8$ s and an energy resolution of 10$^{-9}$ eV. It provides the information on electronic state of Fe, the magnetic structure, and the local crystallographic structure around Fe. There have been already some Mössbauer spectroscopic studies of GaFeO$_3$ [3, 5-7], but they have not focused on its multiferroelectricity. In our previous Mössbauer research with application of a magnetic field ($H_{ex}$) along the $a$-axis, we observed no change in the quadrupole coupling constant ($e^2qQ/2$) in relation with the ME effect [8]. However, we found some characteristic features: extremely larger $e^2qQ/2$ values than those expected form the crystal structure and unexpected increase of the hyperfine field ($H_{hf}$) of Fe1 in applied magnetic field.

In the present research, we have conducted more precisely $^{57}$Fe Mössbauer spectroscopy in an applied magnetic field by using a stoichiometric single crystal. This time, the magnetic field was applied along the $c$- or $b$-axes. We found the change of $e^2qQ/2$ values when the magnetic field was applied along the $c$-axis. This feature seems to be consistent with the theory of toroidal moment.

![Crystal structure of GaFeO$_3$](image1)

**Figure 1.** Crystal structure of GaFeO$_3$ (projection view from the $c$-axis).

![Paramagnetic spectra at RT](image2)

**Figure 2.** Paramagnetic spectra at RT for the case of (a) $γ$ || $c$ and (b) $γ$ || $b$.

### 2. Experiments

$^{57}$Fe Mössbauer spectra were measured in standard transmission geometry using $^{57}$Co-in-Rh (25 and 50 mCi) as $γ$-ray source. $c$-Plane disk (approximately 4 mm diameter and 40 $μ$m thickness) and $b$-plane disk (approximately 3 mm diameter and 50 $μ$m thickness) were used as absorbers. The measurements were conducted at room temperature (RT) and 4.2 K. The directions of incident $γ$-ray were parallel to the $c$- or $b$-axes. A magnetic field of 5 T was also applied parallel to the $c$- or $b$-axes at 4.2 K. The Doppler velocity scale was calibrated by using Fe metal foil at room temperature. Since the asymmetry parameter $η$ is not zero (the site symmetry: 1), we have analyzed the spectra strictly using
3. Results and discussion

The paramagnetic spectra at RT are shown in figures 2 for the case of (a) $\gamma \parallel c$ and (b) $\gamma \parallel b$. Both spectra are composed of asymmetric Fe$^{3+}$ doublets corresponding to those on Fe1, Fe2, and Ga2 sites. In order to assign the three subspectra, we first calculate the electric field gradients (EFG) at Fe nuclei on the basis of the crystal structure. The EFG tensor at the Fe nucleus can be calculated using

$$V_{pq} = \sum_i \gamma_i V^{(i)}.$$

(1)

Here, $(p, q)$ denote $(x, y, z)$, and $V^{(i)}$ denotes the electric potential by the $i$-element. Using the structure parameters [2] and assuming a point charge model (monopole contribution) for $V^{(i)}$, the summation over a lattice (within a 100 Å sphere) gives each $V_{pq}$ component. Diagonalization of the tensor yields the principal components $V_{zz}$ (eigenvalues) and the principal axes (eigenvectors). The electric field gradient sensed by the $^{57}$Fe nucleus $q_{\text{lat}}$ is expressed by

$$q_{\text{lat}} = (1 - \gamma_e) \frac{V_{zz}}{e}.$$

(2)

Here, $\gamma_e$ represents the antishielding factor. Using $\gamma_e = -9.14$ [9] and $Q = 0.187$ barn [10], the quadrupole coupling constant due to the lattice contribution $e^2 q_{\text{lat}} Q/2$ can be calculated. On the other hand, from the direction of the incident $\gamma$ ray with respect to the principal axes, we can obtain the intensity ratio of the second line to the first line of the paramagnetic doublet, $I_2/I_1$. The calculated results are indicated in table 1. Although the calculated $e^2 q_{\text{lat}} Q/2$ values are small to fit the spectra, we regard the calculated $\eta$ and $I_2/I_1$ to be valid and fix them in the analysis. The best-fit curves composed of three subspectra corresponding to Fe$^{3+}$ ions on Fe1, Fe2, and Ga2 sites are indicated in figures 1. The ratio of the three subspectra is kept close to that determined by neutron diffraction (0.77 : 0.70 : 0.35). The resultant parameters, isomer shift $IS$, $e^2 q^{Q}/2$, and line width $W$ are listed in table 2 for the case of $\gamma \parallel c$. Almost the same parameters, within the experimental errors, are also obtained for the case of $\gamma \parallel b$. Note here that the experimental $e^2 q^{Q}/2$ values are extremely larger than the calculated ones (about twice). This is quite unusual for the Fe$^{3+}$ ion. In many Fe$^{3+}$-containing oxides, the calculated values coincide well with the experimental ones [11-14]. There might be a dipole contribution to the EFG [15], but its magnitude is usually 1/10 of that from the monopole contribution.

| Table 1. Calculated paramagnetic parameters, $e^2 q_{\text{lat}} Q/2$, $\eta$, and $I_2/I_1$ for $\gamma \parallel c$ and $\gamma \parallel b$. |
|-----------------|-----------------|-----------------|-----------------|
| site | $e^2 q_{\text{lat}} Q/2$ (mm/s) | $\eta$ | $I_2/I_1$ ($\gamma \parallel c$) | $I_2/I_1$ ($\gamma \parallel b$) |
| Fe1 | 0.246 | 0.54 | 0.66 | 1.67 |
| Fe2 | 0.286 | 0.49 | 0.68 | 0.63 |
| Ga2 | -0.533 | 0.77 | 0.97 | 0.78 |

| Table 2. Obtained paramagnetic parameters, $IS$, $e^2 q^{Q}/2$, and $W$ at RT ($\gamma \parallel c$). |
|-----------------|-----------------|-----------------|-----------------|
| site | $IS$ (mm/s) | $e^2 q^{Q}/2$ (mm/s) | $W$ (mm/s) | ratio |
| Fe1 | 0.355(10) | 0.383(10) | 0.261(10) | 0.40(1) |
| Fe2 | 0.353(10) | 0.634(10) | 0.289(10) | 0.38(1) |
| Ga2 | 0.352(10) | -1.009(10) | 0.235(10) | 0.22(1) |

a mixture of magnetic and quadrupole Hamiltonians. Lorentzian line shapes were assumed for the analysis of the spectra.
Another possible contribution is a spin-orbit interaction, the sign of which is the same as the lattice contribution [16]. We consider that if the spin-orbit interaction exists as a higher-order term (Pryce’s Hamiltonian), it can be one origin of the unexpectedly large $e^2qQ/2$.

The magnetically ordered spectra at 4.2 K are shown in figures 3 for the case of $\gamma \parallel c$ with applied magnetic field of (a) 0 and (b) 5 T (|| c). The obtained parameters, $IS$, $e^2qQ/2$, hyperfine field $H_{hf}$, observed field $H_{obs}$ (only with $H_{ax}$), and outermost line width $W_{16}$ are listed in tables 3 and 4, respectively. $H_{obs}$ in table 4 are obtained from the vector sum relation, $H_{obs} = H_{hf} + H_{ax}$. The spectrum with $H_{ax} = 0$ can be well fitted using the same EFG parameters as those of the paramagnetic spectrum. The small absorption intensities at the second and fifth lines seem to result from the shape anisotropy of the specimen and the geometrical setup of the experiments. On the other hand in the spectrum with $H_{ax} = 5$ T (|| c), $e^2qQ/2$ values of Fe1 and Fe2 sites increase noticeably (that of Ga2 site is assumed unchanged for simplicity). This indicates an increase of the local distortion, possibly by the displacements of Fe ions on Fe1 and Fe2 sites toward $-b$ direction. For example, if we assume the displacements of 0.1Å toward $-b$ direction, $e^2d_{ab}Q/2$ calculated by equations (1) and (2) increase by 40 and 15% for Fe1 and Fe2 sites, respectively. This feature seems to be related to the toroidal moment.

As a reference, we show in figures 4 the magnetically ordered spectra at 4.2 K for the case of $\gamma \parallel b$ with applied magnetic field of (a) 0 and (b) 5 T (|| b). The spectra have been averaged once, since the resolution is not so good due to the shape of the absorber. The magnetic moments are in the $c$-direction when $H_{ax} = 0$, while they are in the $bc$-plane with the angle of about 40º from the $b$-axis when $H_{ax} = 5$ T (|| b). Both spectra can be fitted well using the same EFG parameters as those of the paramagnetic spectrum. That is, no change in $e^2qQ/2$ is observed with $H_{ax} = 5$ T (|| b). This result also seems to support the theory of toroidal moment.

Figure 3. Magnetically ordered spectra at 4.2 K for the case of $\gamma \parallel c$ with applied magnetic field of (a) 0 and (b) 5 T (|| c).
Table 3. Hyperfine parameters, IS, $e^2 q Q / 2$, $H_{hf}$, and $W_{16}$ at 4.2 K in $H_{ex} = 0$ ($γ \parallel c$).

| site | IS (mm/s) | $e^2 q Q / 2$ (mm/s) | $H_{hf}$ (T) | $W_{16}$ (mm/s) | ratio |
|------|-----------|---------------------|--------------|----------------|-------|
| Fe1  | 0.473(10) | 0.383(10)           | 46.8(1)      | 0.538(10)      | 0.40(1) |
| Fe2  | 0.488(10) | 0.634(10)           | 49.3(1)      | 0.385(10)      | 0.38(1) |
| Ga2  | 0.458(10) | -1.009(10)          | 49.3(1)      | 0.383(10)      | 0.22(1) |

Table 4. Hyperfine parameters, IS, $e^2 q Q / 2$, $H_{obs}$, $H_{hf}$, and $W_{16}$ at 4.2 K in $H_{ex} = 5$ T ($γ \parallel c$).

| site | IS (mm/s) | $e^2 q Q / 2$ (mm/s) | $H_{obs}$ (T) | $H_{hf}$ (T) | $W_{16}$ (mm/s) | ratio |
|------|-----------|---------------------|--------------|-------------|----------------|-------|
| Fe1  | 0.459(10) | 0.431(10)           | 52.7(1)      | 47.7(1)     | 0.599(10)      | 0.41(1) |
| Fe2  | 0.467(10) | 1.178(10)           | 44.1(1)      | 49.1(1)     | 0.611(10)      | 0.38(1) |
| Ga2  | 0.475(10) | -1.009(10)          | 44.1(1)      | 49.1(1)     | 0.403(10)      | 0.21(1) |

Figure 4. Magnetically ordered spectra at 4.2 K for the case of $γ \parallel b$ with applied magnetic field of (a) 0 and (b) 5 T ($|| b$).

It is seen from tables 3 and 4 that the magnitudes of $H_{hf}$ are rather small for Fe$^{3+}$ oxides. This corresponds to the neutron diffraction analysis that Fe$^{3+}$ moments are smaller than 5 $µ_B$, i.e., 3.9, 4.5, and 4.7 $µ_B$ for Fe1, Fe2, and Ga2 sites, respectively [2]. The reduction of the magnetic moments may be caused by the Fe 3d – O 2p hybridization depicted by X-ray absorption spectroscopy [17]. Note that $H_{hf}$ of Fe1 increases by $δH_{hf} = 0.9$ T when the magnetic field ($H_{ex} = 5$ T) is applied, while those of Fe2...
and Ga2 sites stay almost unchanged. The same feature is observed in the case of \( H_{\text{dy}} \parallel b \) with \( \delta H_{\text{dy}} \sim 1.5 \, \text{T} \) in Fe1. The difference between the two cases, about 0.6 T, is explained well by the magnetic dipole field. But the rest part, \( \delta H_{\text{dy}} \sim 0.9 \, \text{T} \), cannot be explained by the other factors, such as the magnetic anisotropy, the partial magnetic susceptibility, and the demagnetization field. We consider that this feature may be related to the spin-orbit interaction. The effect of the spin-orbit interaction in this material has been also pointed out in other measurements such as the magnetic anisotropy \([18]\) and the X-ray nonreciprocal directional dichroism \([19]\).

4. Summary

We have conducted Mössbauer spectroscopy in applied magnetic field in order to examine the multiferromagnetic of GaFeO\(_4\). Based on the EFG calculation, reasonable fitting can be obtained for the paramagnetic spectra with the incident \( \gamma \) ray parallel to both the \( c \)- and \( b \)-axes. But \( e^2qQ/2 \) values are unexpectedly large, about twice of the calculated ones, which may be due to the dipole contribution or the spin-orbit interaction. At 4.2 K, \( e^2qQ/2 \) of Fe1 and Fe2 sites increase noticeably only when the magnetic field is applied along the \( c \)-axis, which is suggestive of the displacement of Fe ions toward \(-b\) direction. This feature seems to be related to the toroidal moment. We also found the increase of \( H_{\text{dy}} \) by application of the magnetic field only for Fe1 site. We consider that this may be related to spin-orbit interaction.

Acknowledgement

This work has been carried out in part under the Visiting Researchers Program of Kyoto University Research Reactor Institute. The authors are grateful to Prof. Arima, University of Tokyo, for providing us a stoichiometric single crystal.

References

[1] Remeika J P 1960 J. Appl. Phys. 31 263S
[2] Arima T, Higashiyama D, Kaneko Y, He J P, Goto T, Miyasaka S, Kimura T, Oikawa K, Kamiyama T, Kumai R and Tokura Y 2004 Phys. Rev. B 70 064426
[3] Bertaut E F, Bassi G, Buisson G, Chappert J, Delapalme A, Pauthenet R, Rebouillat H P and R Aleonard 1966 J. Phys. (Paris) 27 433
[4] Popov Y F, Kadomtseva A M, Vorob’ev G P, Timofeeva V A and Ustinin D M 1998 J. Exp. Theor. Phys. 87 146
[5] Frankel R B, Blum N A, Foner S, Freeman A J and Schieber M 1965 Phys.Rev.Lett. 15 958
[6] Trooster J M and Dymanus A 1967 Phys.Stat. Sol. 24 487
[7] Sharma K, Raghavendra Reddy V, Gupta A, Banerjee A and Awasthi A M 2013 J Phys.: Condens. Matter 25 1
[8] Nakamura S, Morimoto S, Saito T and Tsunoda Y 2010 J. Phys. Conf. Ser. 200 012140
[9] Sternheimer R M 1963 Phys. Rev. 130 1423
[10] Stevens J G and Stevens V E 1973 Mössbauer Effect Data Index (New York: Plenum Press) p 60
[11] Obanawa C and Tanaka M 1971 Natural Science Report, Ochanomizu University 22 143
[12] Nakamura S, Fuwa A and Tsunoda Y 2012 Hyperfine Interactions 208 29
[13] Nakamura S and Oikawa K 2003 J. Phys. Soc. Jpn. 72 3123
[14] Nakamura S, Tsunoda Y and Fuwa A 2012 Hyperfine Interactions 208 49
[15] Artman J O 1966 Phys. Rev. 143 541
[16] Ingalls R 1964 Phys. Rev. 133 A787
[17] Kim J Y, Koo T Y and Park J H 2006 Phys. Rev. Lett. 96 047205
[18] Levine B F, Nowlin C H and Jones R V 1968 Phys. Rev. 174 571
[19] Kubota M, Arima T, Kaneko Y, He J P, Yu X Z and Tokura Y 2004 Phys. Rev. Lett. 92 137401