Mössbauer Study on the Polar Ferrimagnet GaFeO$_3$

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Abstract: In order to clarify the origin of magnetostrictive (ME) effect in the polar ferrimagnet GaFeO$_3$, we have conducted Mössbauer spectroscopy by using a stoichiometric single crystal. The spectra are composed of three subspectra, corresponding to Fe$^{3+}$ ions on Fe1, Fe2, and Ga2 sites. The quadrupole splitting ($Q_S$) of Fe1 subspectrum, 1.05 mm/s, is too large to be explained by the electric field gradients (EFG) due to the lattice contribution. At 5K, there is no difference in the quadrupole parameters between the spectrum with and without applied magnetic field, suggesting that the ME effect is not caused by a displacement of ions. Note that in applied magnetic field, Fe1 subspectrum shows extra increase in observed field of about 10kOe. In conjunction with the large $Q_S$, this feature may be due to the spin-orbit interaction, which can also be the cause of the large magnetic anisotropy.

1. Introduction

Gallium iron oxide GaFeO$_3$ has an orthorhombic structure ($Pc2_1n$), which consists of three types of octahedral sites (Fe1, Fe2, and Ga2) and one tetrahedral site (Ga1). The material is piezoelectric with the dielectric moments along $b$-axis and at the same time is ferrimagnetic with the magnetic easy direction of $c$-axis [1]. Bertaut et al proposed three sublattice ferrimagnetic model that Fe$^{3+}$ ions occupy Fe1, Fe2, and Ga2 sites with the occupancy of 0.87, 0.90, and 0.54, respectively [2]. At low temperature GaFeO$_3$ shows magnetostrictive (ME) effect. In general, when the magnetic field or the electric field is applied to the material, ME effect is caused by the change in (1) magnetic interaction due to the displacement of ions, (2) magnetic anisotropy, and (3) $g$-value. Especially in the case (1), Mössbauer quadrupole effect is expected to change because it is very sensitive to the local structure. There are several reports on the Mössbauer spectroscopy of this material [3-5], but the measurements were conducted by using powdered specimens and the analysis by two subspectra approximation.
In order to clarify the origin of the ME effect in GaFeO$_3$, we have applied Mössbauer spectroscopy to a stoichiometric single crystal. We have analyzed the spectrum based on the three sublattice ferrimagnetic model [2], and examined the difference between hyperfine parameters with and without applied magnetic field.

2. Experiments

A stoichiometric single crystal with $a$-plane platelet (about 5mm x 4mm x 80µm size) was used as an absorber. The lattice constants are $a = 8.7442\,\text{Å}$, $b = 9.3927\,\text{Å}$, and $c = 5.0823\,\text{Å}$ at room temperature. The Curie temperature is 200K and the saturation magnetization is $0.7\mu_\text{B}/\text{f.u.}$ at 5K. Details of the sample characterization were described in reference [6]. The $^{57}$Fe Mössbauer spectra were measured in standard transmission geometry for the temperature range from 5K to 293K. As $\gamma$-ray source, $^{57}$Co-in-Rh (25mCi) was used and the Doppler velocity scale was calibrated by using Fe metal foil at room temperature. The direction of incident $\gamma$-ray was parallel to the $a$-axis. The magnetic field up to 50 kOe was also applied parallel to the $a$-axis. Lorentzian line shapes were assumed for the analysis of the spectra.

3. Results and discussions

In figure 1, the paramagnetic spectrum at 293K is shown. The spectrum apparently consists of two subspectra as reported previously [3-5]. Therefore we first calculated the electric field gradients (EFG) at Fe nuclei on Fe1, Fe2, and Ga2 sites due to the lattice contribution by using a point charge model (electric monopole). The calculation yields the quadrupole splittings ($QS$) of 0.23, 0.28, and -0.52 mm/s, respectively. Although these magnitudes themselves do not coincide well with the experimental ones, here we assume the calculated principal axes of EFG to be valid, which determine the intensity ratio ($I_1:I_2$) of each doublet. We also assume the same absorption line width for the three subspectra (0.29(1) mm/s). Therefore the spectrum can be well decomposed into three asymmetric subspectra, corresponding to Fe$^{3+}$ ions on Fe1, Fe2, and Ga2 sites. The quadrupole parameters used to fit the spectrum are indicated in table 1. The quadrupole splittings are 1.05(2), 0.58(2), and -0.38(2) mm/s, respectively and the isomer shifts are 0.35(2), 0.36(2), and 0.35(2) mm/s, respectively. The existence ratio is about 1.0: 1.1: 0.8, almost consistent with that reported by Bertaut [2]. Note that the $QS$ of Fe1 subspectrum is too large to be explained by the EFG due to the lattice contribution.

![Figure 1. Paramagnetic spectrum of GaFeO$_3$ at 293K ($\gamma//a$-axis).](image-url)
Table 1. Quadrupole parameters used to fit the spectrum at 293 K. Here \( \eta \) denotes asymmetric parameter, \( \theta \) and \( \phi \) denote Euler angles of the incident \( \gamma \)-ray direction with respect to the principal axes of EFG.

| site | \( QS \) (mm/s) | \( \eta \) | \( \theta \) (deg) | \( \phi \) (deg) | \( I_1 : I_2 \) |
|------|-----------------|----------|------------------|-----------------|----------------|
| Fe1  | 1.05(2)         | 0.5      | 60               | 250             | 1 : 0.76       |
| Fe2  | 0.58(2)         | 0.6      | 5                | 90              | 1 : 2.75       |
| Ga2  | -0.38(2)        | 0.5      | 30               | 200             | 1 : 0.48       |

In figure 2, the magnetically ordered spectrum at 5K is shown. The spectrum can be well analyzed as superposition of the three subspectra with the quadrupole parameters at 293K and with the hyperfine fields along the \( c \)-axis. The isomer shifts are all 0.49(2) mm/s, and the hyperfine fields are 470(2), 490(2), and 490(2) kOe, for Fe1, Fe2, and Ga2 sites, respectively. The outermost line widths are all 0.50(2) mm/s.

Figure 2. Magnetically ordered spectrum of GaFeO\(_3\) at 5K (\( \gamma//a \)-axis).

In figure 3, the spectrum at 5K in applied magnetic field is shown. The subspectra corresponding to up-moment (Fe\(^{3+}\) on Fe2 and Ga2 sites) and that to down–moment (Fe\(^{3+}\) on Fe1 site) separate clearly each other. The 2-5 lines still remain some extent, indicating that the magnetic moments do not align parallel to the direction of applied magnetic field due to the strong magnetic anisotropy [7]. The spectrum can be well fitted by using the same quadrupole parameters as those in zero-field spectrum (figure 2) and by assuming that the moments cant about 25 degrees from the \( a \)-axis toward the \( c \)-axis. Although the material shows clear ME effect at 5K in applied magnetic field of 50kOe [6], there is no difference in the quadrupole parameters between these two spectra (without and with applied magnetic field). This suggests that the ME effect is not caused by a displacement of ions. In table 2, the values of hyperfine field (without applied magnetic field) and observed field (with applied magnetic field) are indicated for each site. The observed field should be the vector sum of the hyperfine field and the applied field. It is noted that in applied magnetic field, Fe1 subspectrum has an extra increase in observed field. Even if taking both the magnetic anisotropy and the magnetic dipole field into account,
the increase of about 10kOe cannot be explained. In conjunction with the large quadrupole splitting, this feature may be due to the spin-orbit interaction, which can also be the cause of the unexpectedly large magnetic anisotropy [8]. We consider that the origin of the ME effect in this material may lie in this point.

For further investigations, we are planning to conduct measurement in applied magnetic field along the $c$-axis.

![Graph](image)

**Figure 3.** Magnetically ordered spectrum of GaFeO$_3$ at 5K in applied magnetic field of 50kOe ($\gamma$// $a$-axis, $H_{ap}$/ $a$-axis)

**Table 2.** The values of hyperfine field $H_{hf}$ (without applied magnetic field) and observed field $H_{obs}$ (with applied magnetic field) at 5 K.

| site | $H_{hf}$ (kOe) | $H_{obs}$ (kOe) |
|------|---------------|-----------------|
| Fe1  | 470(2)        | 530(2)          |
| Fe2  | 490(2)        | 448(2)          |
| Ga2  | 490(2)        | 448(2)          |

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