Element-specific magnetic hysteresis loops observed in hexagonal ErFeO$_3$ thin films

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Abstract

We investigated the magnetic properties of multiferroic hexagonal ErFeO$_3$ thin films by using x-ray magnetic circular dichroism (XMCD) and synchrotron Mössbauer spectroscopy. In order to reveal the element-specific magnetic properties, temperature-dependent XMCD experiments were conducted at the Fe $L_{2,3}$ and Er $M_{4,5}$-edges. Apparent magnetic hysteresis loops appear for both ions below the Néel temperature, which suggests the existence of ferromagnetism. The temperature evolutions of the coercive field and spontaneous magnetization for both ions show similar behavior. These results indicate that Fe ions influence the magnetism of Er ions. Our results deepen the understanding of the physical properties of hexagonal rare-earth ferrite system.

1. Introduction

Multiferroics which possess more than two ferroic order parameters in the same phase have been intensively studied from the viewpoints of fundamental research and applications [1, 2]. It has been expected for a long time that multiferroics will make a breakthrough in spintronics and memory devices due to the magnetoelectric effect [3]. To achieve this aim, it is important to show multiferroic properties at room temperature. However, the number of such multiferroics is limited because of the contradictory requirements for magnetic and ferroelectric properties. For typical ferroelectrics with ABO$_3$ perovskite structures, atomic displacements prefer to have an empty $d$ orbital for B site cations, which does not induce magnetism due to the lack of a partially filled $d$ orbital. However, when the B site cation has $d$ electrons, it suppresses the ferroelectric distortion [4]. These facts make it difficult to realize the coexistence of ferroelectricity and magnetism in a single phase. To avoid this difficulty, new approaches to realize multiferroics have been proposed [5]. One direction is the use of so-called type I multiferroics such as hexagonal YMnO$_3$ [6], where ferroelectricity and magnetism have different origins. Type I multiferroics normally exhibit a large polarization with a high transition temperature, while the magnetoelectric coupling is rather weak. Another direction is the use of so-called type II multiferroics. Type II multiferroics have strong magnetoelectric coupling since ferroelectricity is induced by spin ordering [7]. However, the ferroelectric phase only appears at very low temperature with a very small polarization.

Hexagonal rare-earth ferrite (h-RFeO$_3$) is an attractive material that has been found to be multiferroic at room temperature [8–12]. Additionally, a linear magnetoelectric effect has been predicted in these compounds [13]. Despite the aforementioned situation, the h-RFeO$_3$ family has not been well studied due to their difficult synthesis [8, 9, 14–16]. Mostly, RFeO$_3$ is stable in an orthorhombic perovskite structure and the hexagonal structure only exists as a metastable phase. One of the most promising methods to realize a metastable hexagonal phase is to synthesize a thin film using the metal organic chemical vapor deposition (MOCVD) [8, 17] and the pulsed laser deposition (PLD) [18–20] technique. Using these methods, h-RFeO$_3$ samples with various rare-earth ions have been successfully obtained, and their physical properties have been reported.
As previously demonstrated, the h-ErFeO₃ thin film exhibits ferroelectric and weak ferromagnetic properties below the Néel temperature [21]. The magnetic ordering of Fe ions in the h-ErFeO₃ thin film was revealed by using Mössbauer spectroscopy. However, information on the contribution from rare-earth ions is still lacking. In the h-Fe₂O₃ system, it is predicted that the ionic size of rare earth component affects the magnitude of electric polarization and the magnetic transition by first-principle calculations [22]. Therefore, it is important to elucidate its contribution to the physical properties.

In the present paper, we synthesized a h-ErFeO₃ thin film, and its magnetic properties were examined by soft x-ray magnetic circular dichroism (XMCD) spectroscopy. XMCD is a very powerful tool that enables us to separate the contribution from different magnetic ions. Using this technique, we can evaluate the contributions of rare-earth ions to the magnetic properties. Since XMCD is surface-sensitive, we also conducted synchrotron Mössbauer spectroscopy by using the ⁵⁷Fe probe layer method [23] to investigate the local structures near the surface compared with those in bulk h-ErFeO₃ [21].

2. Experimental

Hexagonal ErFeO₃ thin films (h-ErFeO₃) were grown on yttria stabilized zirconia (YSZ) (111) substrates by the PLD technique. An Nd:YVO₄ laser with fourth harmonics of 266 nm wavelength, and a frequency of 10 Hz was employed. Orthorhombic ErFeO₃ ceramic targets were prepared by a solid-state reaction from Er₂O₃ and Fe₂O₃ powders. h-ErFeO₃ thin films were fabricated under the following conditions: an oxygen pressure of 300 mTorr and a substrate temperature of 850 °C. The obtained thin films were characterized by the x-ray diffraction with a Cu Kα, radiation source. The θ − 2θ scan, ϕ scan and asymmetric θ − 2θ scan were conducted, and the epitaxial growth of the c-axis oriented h-ErFeO₃ thin film with the [1 1 0] direction parallel to the [1 1 0] direction of the YSZ substrate was confirmed.

Element-specific x-ray absorption spectroscopy (XAS) and element-specific x-ray magnetic circular dichroism (XMCD) measurements at the Er M₄,5-edge and the Fe L₂,₃-edge were performed at BL-16A of the Photon Factory in the High Energy Accelerator Research Organization (KEK) and at BL23SU [24] in SPring-8. The soft x-ray measurements were taken in the total electron yield mode with a probing depth of several nm. All spectra were measured with circularly polarized light. Since h-ErFeO₃ thin films are insulators, a Pt electrode with a thickness of 2 nm was deposited onto the film surface to make an electrical contact. A magnetic field was applied along the hexagonal c-axis of the thin film, which corresponds to the easy magnetization axis. The SQUID measurement shows that the magnetic moment does not flip in an in-plane magnetic field of up to 5 T. The incident angle of the x-ray was fixed parallel to the c-axis of the thin film. XAS spectra with different helicities were collected at 5.5, 20, 50, 100 and 120 K for both the Er M₄,5-edge (from 1380 to 1450 eV) and the Fe L₂,₃-edge (from 685 to 750 eV) under a magnetic field of T. We also investigated the magnetic field dependences at 5.5, 7, 8, 10, 20, 50, 75, 100, 120 and 150 K. Since the XMCD is surface sensitive, grazing incidence synchrotron radiation Mössbauer spectroscopy was performed at beamline BL11XU of SPring-8 for a comparison. ⁵⁷Fe Mössbauer spectra were measured using a ⁵⁷FeBO₃ (111) nuclear Bragg monochromator under total reflection conditions. The π-polarized ⁵⁷Fe-SR-Mössbauer radiation (λ = 0.86 Å for the 14.4 keV nuclear resonance energy of ⁵⁷Fe) with an extremely narrow bandwidth of 15.4 neV was filtered from Sr The experimental details are described in [25] and [23]. The monochrometric beam was incident into a h-ErFeO₃ thin film with a grazing angle of either 0.16 or 0.13°. To obtain enough signals, we prepared a h-ErFeO₃ thin film with a 2 nm ⁵⁷Fe-enriched layer (corresponding to two unit cells) embedded to a depth of 2 nm below the surface. The Mössbauer spectra were collected at 5.7, 30, 110, 150, and 200 K using a NaI scintillation detector.

3. Results and discussions

3.1. XMCD spectra

Figures 1(a) and (b) show the XAS spectra of Er M₄,5-edge and Fe L₂,₃-edge measured at 5.5 K, respectively. The XAS spectra are obtained as the sum spectra of different helicities and each spectrum is normalized by the maximum intensity. A 2:1 L₃/L₂ edge jump and 2nd order diffraction of the Er M₄,5-edge are subtracted from all Fe L₂,₃-edge data before normalization. Since the 2nd order diffraction of the Er M₅-edge is well separated from the Fe L₂,₃-edge, we rescaled our XAS spectra of the Er M₄,5-edge and subtracted them from the Fe XAS spectra. For the Er M₄,5-edge, almost the same XAS spectra are obtained for other temperatures. The spectrum shows good agreement with the theoretical dipole excitation spectrum of the ground level from the Hund’s rule [26]. The M₅-edge exhibits a characteristic triplet profile, which has been reported in other Er compounds. This triplet peak originates from the optical selection rules ΔJ = 0, ± 1. Regarding the M₄-edge, splitting is not visible since this contribution is more obvious in the 3d₅/₂ group for Er ions. In the case of the Fe L₂,₃-edge, the
spectrum shape is different from $\alpha$-Fe$_2$O$_3$ or $\gamma$-Fe$_2$O$_3$ which has $O_h$ Fe$^{3+}$ site or a mixture of $O_h$ and $T_d$ Fe$^{3+}$ sites \[27\]. This result is not surprising since Fe$^{3+}$ has a coordination number of five to form corner-linked fivefold trigonal bipyramids and is located at a low symmetry site \[6\]. The point group of the Fe$^{3+}$ site is lower than $D_{3h}$ with energy splitting of $a''_1$, $e'$, and $e''$. This energy splitting explains our XAS spectra and similar profiles have been reported in other materials \[28, 29\]. Figures 1(c) and (d) exhibit the XAS spectra of Er and Fe for different helicities measured at 5.5 K, respectively. The $M_5$-edge shows a large difference, which produces a strong XMCD results, as shown in figure 1(e). The obtained XMCD spectra are similar to the Er XMCD spectra observed in metallic systems. Although the difference between each helicity for the Fe spectra is much smaller than that of the Er $M_5$-edge, it exhibits a distinct difference, and the XMCD spectrum is shown in figure 1(f). Although the obtained Fe $L_3$-edge XMCD spectra having two positive peaks and a negative peak are similar to those of the $h$-YbFeO$_3$ thin film \[28\], this characteristic profile has also been reported in materials containing more than two Fe sites \[30\]. This result suggests the possibility of having two sites for Fe ions. Further experiments are needed to clarify this point. The temperature dependences of the XMCD spectra for Er and Fe are summarized in figure 2. The obtained features of the XMCD spectra do not change as a function of temperature. With an increasing temperature, the magnitude of the XMCD intensity decreases monotonically and becomes almost zero above the Néel temperature of 120 K. This phase transition temperature coincides well with previously reported SQUID measurement \[21\]. The negative sign of the XMCD in the $L_3$ edge for Fe ions indicates that the spin moment direction is parallel to the external magnetic field.

Figure 1. XAS spectra of the $h$-ErFeO$_3$ thin film measured at 5.5 K in a magnetic field of 2 T. (a) Er $M_{4,5}$-edge and (b) Fe $L_{2,3}$-edge. Each spectrum is normalized by the maximum intensity. XAS spectra with the different helicities of Er and Fe are shown in (c) and (d), respectively. (e) and (f) XMCD spectra for Er and Fe obtained at 5.5 K, respectively.

Figure 2. XMCD spectra of the $h$-ErFeO$_3$ thin film measured at various temperatures in a magnetic field of 2 T: (a) Er and (b) Fe. XMCD spectra are obtained as a difference of the XAS spectra with different helicities, which are normalized for each temperature.
Using sum-rule analysis, the ratio of the orbital moment \((m_o)\) to spin \((m_s)\) can be obtained from the XMCD spectrum and its integration spectrum \([26, 31–35]\). According to the XMCD sum rules, the orbital and spin magnetic moments for the Fe 3d state can be determined. Since we did not measure the incident angle dependence of XMCD, we cannot obtain the exact value of the angular-dependent magnetic dipole moment. Therefore, we only calculate \(m_o\) by using the following equation:

\[
m_o = - \frac{4}{3} \int_{L_2+L_3} \omega \left( \mu^+ - \mu^- \right) (10 - n),
\]

where \(n\) is the 3d electron occupation number and we assumed that \(n = 5\). The obtained \(m_o\) values are summarized in Table 1. The magnitude of \(m_o\) decreases with temperature. It can be seen that \(m_o\) for Fe is relatively small over the whole temperature range. Such a small value is reasonable and reported in many Fe systems since the ionic state of Fe\(^{3+}\) is half-filled \([36–39]\). To understand the precise contribution from the spin, it is necessary to conduct angular dependence experiments. We also applied the sum rules for the Er 4f state. The obtained \(m_o\) values are tabulated in Table 1 assuming that \(n = 11\). The \(m_o\) value of Er decreases monotonically with an increasing temperature. The inverse of the orbital moment for Er obeys the Curie-Weiss law with the Curie temperature of \(-12.7\) K. This temperature coincides well with the paramagnetic component obtained from a superconducting quantum interference device magnetometer (SQUID) experiment \([21]\). This suggests the possibility that the paramagnetic component that we have observed in the SQUID experiments originates from the Er ion.

Figures 3(a) and (b) show the magnetic field dependences of the XMCD intensity. At 150 K, both Er and Fe ions exhibit linear behaviors which are typical for paramagnetic materials. Below 120 K, the magnetic field dependences behave differently for the Er and Fe ions. Fe exhibits obvious hysteresis loops below 120 K. With a decreasing temperature, the magnetization and the coercive field \(H_c\) increase monotonically until 50 K, which indicates the existence of ferromagnetism along the c-axis. Below 20 K, the shapes of the magnetic hysteresis loops show sudden changes, and the coercive field decreases with a decreasing temperature. However, the Er ion still contains a paramagnetic linear component with an apparent magnetic hysteresis loop below 120 K. This result leads to the conclusion that the paramagnetic contribution that appears in macroscopic measurements is caused by the Er ion. After subtracting the linear component \(\chi H\) at different temperatures, it exhibits well-saturated hysteresis loops in the temperature range of 10 to 75 K. Figure 3(e) shows the temperature dependence of the coercive field for both the Fe and Er ions. Regarding Er ions, we plotted the values obtained from the subtracted hysteresis loops. The magnitude of the coercive field for Er ions takes the same value as that of Fe ions. Figures 3(c) and (d) show the magnitudes of XMCD intensity for the Fe and Er ions obtained at 1 T, respectively. We also collected XMCD intensity as a function of temperature at several different energies (695, 708.7, 740 eV for Fe L\(_3\)-edge and 1380, 1402, 1425 eV for Er M\(_{4,5}\)-edge) and plotted them on the same figures. Fe ions exhibit a maximum value at 20 K and further decreasing the temperature weakens the XMCD intensity. On the other hand, the XMCD intensity of Er ion monotonically increases with a decreasing temperature. Such a difference is derived from a paramagnetic linear component of the Er ion. Since the XMCD intensity corresponds to the magnetic moment, the magnitude of XMCD intensity obtained at 0 T which represents the spontaneous magnetization is plotted in Figure 3(f). Regarding Er ions, these values are calculated from the subtracted hysteresis loops. After subtraction, the behavior of Er is similar to that of Fe ions. These results suggest that the magnetic properties of Er ions are strongly influenced by the Fe magnetic moment through the exchange field, which makes the magnetic ordering temperature of Er higher than that of normal rare-earth containing materials. Another thing that we would like to mention is the directions of the overall magnetic moments for both elements. On the \(h\)-YbFeO\(_3\) thin film, spontaneous magnetization reversal is observed by several authors and explains this phenomenon as the result of the cancellation of the magnetic moment \([19, 28]\), which is different from our current situation. The Dzialoshinskii-Moriya interaction induces the canting of Fe ions from

**Table 1.** Measured orbital moments of the Fe and Er ions in the \(h\)-ErFeO\(_3\) thin film.

|     | Fe         | Er         |
|-----|------------|------------|
|     | \(m_o [\mu_B]\) | \(m_o [\mu_B]\) |
| 5 K | 0.0351     | 1.290      |
| 20 K| 0.0114     | 0.7699     |
| 50 K| 0.0145     | 0.4005     |
| 100 K | -0.0040  | 0.2175     |
| 120 K| 0.0003     | 0.1848     |

\(H_c\) decreases with a decreasing temperature. It can be seen that \(H_c\) for Fe is relatively small over the whole temperature range. Such a small value is reasonable and reported in many Fe systems since the ionic state of Fe\(^{3+}\) is half-filled \([36–39]\). To understand the precise contribution from the spin, it is necessary to conduct angular dependence experiments. We also applied the sum rules for the Er 4f state. The obtained \(m_o\) values are tabulated in Table 1 assuming that \(n = 11\). The \(m_o\) value of Er decreases monotonically with an increasing temperature. The inverse of the orbital moment for Er obeys the Curie-Weiss law with the Curie temperature of \(-12.7\) K. This temperature coincides well with the paramagnetic component obtained from a superconducting quantum interference device magnetometer (SQUID) experiment \([21]\). This suggests the possibility that the paramagnetic component that we have observed in the SQUID experiments originates from the Er ion.

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the \(ab\) plane, which creates an exchange field on the Er ion. This exchange field causes the canting of the Er ion. As a result, the magnetic moments of Er and Fe cant in the same direction from the \(ab\) plane and produce weak ferromagnetism. This model is consistent with previous SQUID and Mössbauer experiments [21]. Mössbauer spectroscopy suggests that the magnetic moment of Fe ions is inclined around 10° from \(ab\) plane at 5 K. Since \(\text{Fe}^{3+}\) ion possesses a magnetic moment of 5 \(\mu_B\), such a canting produces around 0.87 \(\mu_B\)/f.u. along the \(c\)-axis, which is lower than the magnetization obtained from SQUID experiment (shown in figure 3(g)). It means that Er ion is also inclined from the \(ab\) plane and aligned parallel to the Fe ion. A sudden change in the shape of the hysteresis loop probably originates from a strong anisotropy that has the easy magnetization axis along the in-plane direction. To understand the spin configuration of \(h\)-ErFeO\(_3\), DFT calculation is desired and we are planning to perform it and publish the result in elsewhere.

### 3.2. Mössbauer spectra

Figure 4 shows the Mössbauer spectra measured at different temperatures. Paramagnetic spectra consisting of a doublet are observed above 150 K. The isomer shift and quadrupole splitting are 0.37 and 2.01 mm s\(^{-1}\), respectively. The value of the isomer shift suggests that the Fe ions are in a high-spin \(\text{Fe}^{3+}\) state. With decreasing temperature, the Mössbauer spectrum starts to change its shape below 110 K. This temperature coincides well with the XMCD experiments. Below 30 K, well-resolved magnetically ordered spectra with a hyperfine field of 43.3 T at 5.7 K are observed. Although the \(M-H\) hysteresis loops of Er and Fe ions obtained from XMCD measurements show drastic changes below 20 K, there is almost no difference between 30 and 5.7 K. This means that the magnetic structure does not change at approximately 20 K. The intensity ratio of the six absorption lines at 5.7 K is close to 3:4:1:1:4:3, which indicates that the hyperfine field lies approximately in the plane of the film. All these results are quite similar to previously reported work which used a 98% \(^{57}\text{Fe}\)-enriched ErFeO\(_3\) thin film [21]. This result clearly suggests that at a depth of 2 nm below the surface, the magnetic properties and structure
are already recovered to be the same as those in the bulk $h$-ErFeO$_3$. Therefore, we can conclude that the current XMCD data obtained in the total electron yield mode with a larger probing depth reflect the bulk property. In the bulk $h$-ErFeO$_3$, the direction of the magnetic moment of Fe on the same $c$-plane forms a triangular lattice and its magnetization is cancelled. The magnetic moment is canted from the $ab$ plane at 10°, which produces weak ferromagnetism along the $c$-axis. The same picture can be applied for the present study and it agrees with our XMCD results.

4. Conclusions

We have investigated the magnetic properties of $h$-ErFeO$_3$ thin films by using element-specific XMCD and Mössbauer spectroscopy. Well-defined XMCD spectra were observed below the Néel temperature of Er and Fe ions, suggesting the existence of ferromagnetic components for both elements. Both the Er and Fe ions exhibited clear magnetic hysteresis loops below the Néel temperature. For Er ions, it also exhibits the paramagnetic contribution. The magnetic moment and the coercive field exhibited maximum values at 20 K, which was consistent with the SQUID experiment. The exchange field on Er, which is generated by Fe ions, tended to cant the magnetic moment of Er in the same direction. The decrease in the magnitude of the magnetic moment and coercive field could be explained by the change in anisotropy. Mössbauer spectroscopy supported that the magnetic property that we observed this time originated from the bulk effect.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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