

Thickness dependence of Morin transition temperature in iridium-doped hematite layers studied through nuclear resonant scattering

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Published online: 15 November 2017

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Abstract The Morin transition of very thin Ir-doped α -Fe₂O₃ films, which is not detectable with conventional magnetization measurements, was studied by conversion electron Mössbauer spectroscopy using a ⁵⁷Co source and nuclear resonant scattering using a synchrotron light source. It was found that (i) the Morin transition temperature increases as the Ir ratio increases, (ii) it decreases when the film thickness decreases, and (iii) the transition becomes irreversible when Ir ratio is small and the thickness is thin. These tendencies were found reproducible and systematic, although the mechanisms are to be clarified by further studies.

Keywords Mössbauer spectroscopy · Nuclear resonant scattering · Thin films · Antiferromagnet · Magnetic anisotropy · Hematite · Morin transition

1 Introduction

In magnetic recording and spintronics devices, antiferromagnetic layers are often used to pin the magnetization direction of ferromagnetic layers through the interfacial magnetic coupling. In the recent trend to use ferromagnetic layers with perpendicular magnetization for such devices, a variety of antiferromagnetic layers with perpendicular magnetic moments

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2017), Saint-Petersburg, Russia, 3-8 September 2017*
Edited by Valentin Semenov

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are required to be developed. Antiferromagnetic hematite (α -Fe₂O₃) layers grown with the hexagonal (0001) orientation are one candidate for such materials. The magnetic moments of pure α -Fe₂O₃ align along the hexagonal c-axis at low temperatures, but turn to the c-plane when the temperature becomes higher than the Morin transition temperature, which is 263 K in pure bulk samples. If the Morin transition temperature in α -Fe₂O₃(0001) films is raised above room temperature to the practical device-operation temperatures, by means of element doping or some other methods, the films become useful for device applications. Usually for bulk samples, the Morin transition can be detected from temperature dependence of magnetization [1], and also from Mössbauer spectra through temperature dependence of the quadrupole shift in magnetically-split sextet patterns [2, 3].

One method to increase the Morin transition temperature of α -Fe₂O₃ is doping heavy metals such as iridium (Ir) to α -Fe₂O₃ [4–6]. However, the Morin transition temperature of thin α -Fe₂O₃ layer with the thickness below 100 nm has not been studied much because of experimental difficulty to examine the magnetism of very thin antiferromagnetic films grown on single crystal substrates. We report here the thickness dependence of the Morin transition temperature of epitaxial Ir-doped α -Fe₂O₃(0001) layers on Al₂O₃(0001) substrates prepared by a pulsed laser deposition method. The thickness region is below 20 nm, which is the region required for practical spintronics devices. We have applied conversion electron Mössbauer spectroscopy (CEMS) with a ⁵⁷Co source at room temperature to confirm the magnetic properties of thin α -Fe₂O₃ (0001) layers, as in a previous study for thicker films prepared by a sputtering method [6]. At higher temperature range where CEMS with a ⁵⁷Co source becomes more difficult to be applied, we have applied nuclear resonant scattering with the time-domain measurements.

It was confirmed that the Morin transition temperature is raised above room temperature only with 0.5%-Ir doping, and it increases as the amount of doped Ir increases. It was also found that the transition temperature decreases as the layer thickness decreases. We have systematically examined the doping conditions where the perpendicular magnetic moments are realized with the minimum layer thickness in the temperature range required for practical use.

2 Experiments

The Ir-doped α -Fe₂O₃(0001) films were grown on Al₂O₃(0001) substrates using a pulsed laser deposition method. Mixtures of fine α -Fe₂O₃ (non-enriched) and IrO₂ powders with the molar ratio of 99: 1, 98: 2, 95: 5, 90: 10, where the atomic ratios Ir/(Fe + Ir) nominally correspond to 0.5, 1.0, 2.6, and 5.3%, respectively, were sintered and used as the deposition sources. The background oxygen pressure during the deposition was set to 10 Pa, and the substrate temperature was kept at 300 °C. The sources were ablated by YAG laser in double frequency ($\lambda = 532$ nm) with the pulse repetition rate of 30 Hz and the energy density of 1 J/cm². Films with the thickness of 5, 10, and 20 nm were grown with different Ir ratios (0.5, 1.0, 2.6, and 5.3%). The epitaxial growth of hexagonal (0001) orientation with the corundum structure was confirmed by X-ray diffraction measurements.

For some representative samples, CEMS measurements were performed using a ⁵⁷Co source (1,850 MBq or less) at room temperature to check the detailed feature of the Fe environments. The direction of magnetic hyperfine field, which is antiparallel to the local magnetic moment of the antiferromagnetic α -Fe₂O₃, can be examined from the intensity ratio and the quadrupole shift of magnetically-split sextet patterns. Nuclear resonant scattering experiments with a synchrotron light source were performed for a larger number of

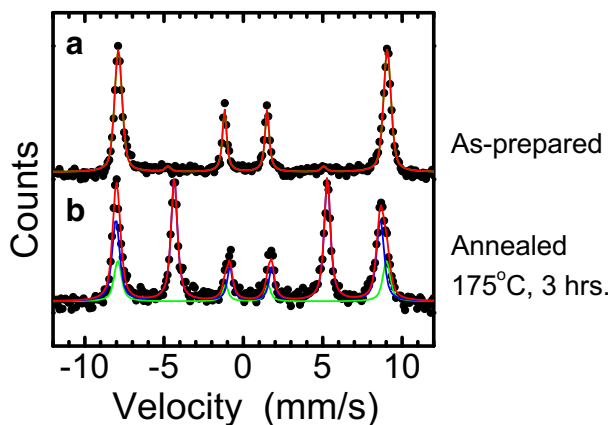


Fig. 1 **a** Conversion electron Mössbauer spectrum of Ir 1.0%-doped α -Fe₂O₃(20 nm) film at room temperature measured using a ⁵⁷Co source. The effect was 1.2%, so that the conversion electron counts were accumulated for 21 days. **b** Spectrum at room temperature after annealed at 175 °C for 3 h. The effect was 0.6% and the counts were accumulated for 27 days. The fitting results are shown by the solid lines for both spectra and the obtained hyperfine parameters are summarized in Table 1

samples at the beamline BL09XU in SPring-8. Pulsed X-rays with the energy of 14.4 keV were made incident on the film samples with the grazing angle geometry, and X-rays resonantly scattered by the ⁵⁷Fe nuclei in the sample were counted by an avalanche photo diode detector as a function of time [7]. From the patterns of the recorded time-spectra the direction of magnetic hyperfine field, whether it is parallel or perpendicular to the film plane, can be obtained [8]. The nuclear resonant scattering experiment makes it possible to examine the direction of magnetic moment of thin films quickly, and to measure it at high temperatures easier, in comparison with the CEMS measurements using a radioisotope γ -ray source. Note that we also have a choice to measure energy-domain spectra of α -Fe₂O₃ using a synchrotron Mössbauer source created by a nuclear Bragg monochromator [9], but in this work we have chosen the time-spectrum method for quicker measurements.

3 Results and discussion

Figure 1a shows the conversion electron Mössbauer spectrum of Ir 1.0%-doped α -Fe₂O₃(20 nm) film at room temperature measured using a ⁵⁷Co source (\sim 1,000 MBq). The effect was only 1.2%, so that the conversion electron counts were accumulated for 21 days. The incident γ -ray direction was set along the film normal, so that the intensity ratio of the sextet, which is nearly 3: 0: 1: 1: 0: 3, means that the direction of the magnetic hyperfine field is perpendicular to the film plane. The hyperfine parameters obtained by fitting the spectrum are shown in Table 1. The positive sign of the quadrupole shift also shows that the direction of the magnetic hyperfine field is parallel to the direction of the electric field gradient, which is parallel to the hexagonal $\langle 0001 \rangle$ direction grown along the film normal. These results mean that the Morin transition temperature of this film is raised above room temperature and an antiferromagnetic film with perpendicular magnetic moments is realized at room temperature with this Ir ratio and thickness. Coexistence of divalent Fe, as in the α -Fe₂O₃-FeTiO₃ system [10], was not observed even for the Ir 5.3%-doped samples.

Table 1 Hyperfine parameters obtained by fitting the Mössbauer spectra shown in Fig. 1

Sample	δ (mm/s)	2ε (mm/s)	B_{hf} (T)	x	Area (%)
As-deposited	0.38	0.44	52.6	0.10	100.0
Annealed at 175 °C	0.38 ^a	-0.17 ^a	51.7	4.00 ^b	80.0
	0.38 ^a	0.34 ^a	52.5	0.00 ^b	20.0

δ : isomer shift, 2ε : quadrupole shift, B_{hf} : magnetic hyperfine field, x : intensity ratio of the 2nd and 5th peaks of the sextet with the notation of 3: x : 1: 1: x : 3

^aConnected parameters

^bFixed parameters

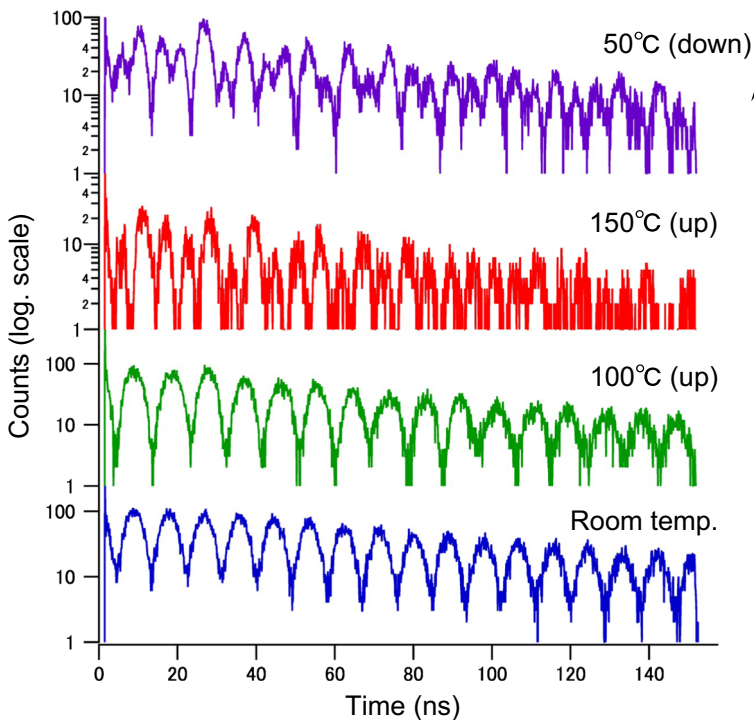


Fig. 2 Nuclear resonant time spectra for Ir 1.0%-doped α -Fe₂O₃(20 nm) film measured at 27 °C (room temperature), 100 °C (heating-up), 150 °C (heating-up), and 50 °C (cooling-down), from the bottom to the top. The measurement time was typically 3 hours per spectrum

In order to evaluate the Morin transition temperature, which is raised above room temperature, nuclear resonant scattering measurements using a synchrotron light source were performed at higher temperatures. Figure 2 shows the nuclear resonant time spectra for Ir 1.0%-doped α -Fe₂O₃(20 nm) film. The measurement time was typically 3 hours per spectrum. The spectrum at room temperature shows a simple quantum beat pattern with a single frequency. This means that the magnetic hyperfine field in this sample is perpendicular to the film plane [8], which is consistent with the CEMS measurement. The spectrum shows the same feature at 100 °C, but drastically changes at 150 °C. This result means that the

Table 2 Morin transition temperature for the samples with different Ir ratio and different thickness determined from the nuclear resonant scattering measurements

	5 nm thick	10 nm thick	20 nm thick
Ir 0.5%			50 ~ 75 °C
Ir 1.0%	75 ~ 100 °C	75 ~ 100 °C	100 ~ 150 °C
Ir 2.6%	75 ~ 100 °C	100 ~ 125 °C	125 ~ 150 °C
Ir 5.3%	125 ~ 150 °C	175 ~ 200 °C	

direction of the magnetic moments changes from perpendicular to parallel with the film plane between these measurement temperatures, i. e., the Morin transition temperature is between 100 and 150 °C. When the temperature is decreased again to 50 °C, the spectrum did not show the same feature as that at room temperature before the Morin transition. The pattern at 50 °C suggests that perpendicular magnetic moments and in-plane magnetic moments coexist in the film, so that the Morin transition appears to be partially irreversible. Such an irreversible transition has not been observed in bulk Ir-doped α -Fe₂O₃ so that it is regarded as a phenomenon proper to very thin films.

Table 2 shows the Morin transition temperatures determined from the nuclear resonant scattering measurements. The transition temperature systematically increases with the increase of the Ir ratio, and decreases with the decrease of the thickness. Table 3 shows the temperature dependence of the direction of magnetic moments for all the measured samples. After the Morin transition took place, the temperature was decreased to 50 °C and the time-spectrum was measured again, to check whether the transition was reversible or irreversible. If it turned out to be reversible, the temperature was increased again to a higher temperature by a step of 25 °C, and reversibility was confirmed repeatedly at 50 °C. The terms “Rev.” and “Irrev.” below the in-plane (horizontal) arrows in Table 3 mean that the transition was found reversible and irreversible, respectively. The irreversible phenomenon was observed only when the Ir ratio is small and the thickness is thin.

The irreversible phenomenon was confirmed also by room-temperature CEMS measurements. Figure 1b shows conversion electron Mössbauer spectrum of Ir 1.0%-doped α -Fe₂O₃ (20 nm) film at room temperature after annealed at 175 °C for 3 hours. The effect was 0.6% and the counts were accumulated for 27 days. The intensity ratio of the sextet is nearly 3: 3: 1: 1: 3: 3, suggesting that the Fe sites with in-plane magnetic moments are dominant. The spectrum was fitted with a component with in-plane magnetic moments, which have the intensity ratio of 3: 4: 1: 1: 4: 3 and a negative quadrupole shift, and a component with perpendicular magnetic moments, which have the intensity ratio of 3: 0: 1: 1: 0: 3 and a positive quadrupole shift, as in the spectrum analyzes for bulk single crystal α -Fe₂O₃ [11]. The hyperfine parameters obtained by fitting are summarized in Table 1. From the area ratio of the two components, it was found that 80% of α -Fe₂O₃ has an irreversible feature but 20% has a reversible feature. Note that the CEMS pattern at room temperature after annealed at 125 °C, which is just above the Morin transition temperature determined by the nuclear resonant scattering measurements showed a sextet with the intensity ratio close to 3: 0: 1: 1: 0: 3, indicating no sign of irreversibility at this annealing temperature.

The tendency that the Morin transition temperature increases as a function of the Ir ratio is the same as the reported results on single crystal [4] and particles [5]. The Morin transition occurs as a result of competition between the single ionic magnetic anisotropy, which favors antiferromagnetic structure with c-axis-oriented magnetic moments and dominates at lower temperatures, and the dipolar magnetic anisotropy, which favors antiferromagnetic

Table 3 Direction of magnetic moments as a function of temperature

Ir ratio (%)	Thickness (nm)	27 °C	50 °C	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C	250 °C	300 °C
0.5	20	↑	↑	→	→						
				Rev.	Irrev.						
1.0	5	↑	↑	↑	→						
					Irrev.						
	10	↑	↑	↑	→						
					Irrev.						
	20	↑			↑		→				
							Irrev.				
2.6	5	↑	↑	↑	→	→					
					Rev.	Irrev.					
	10	↑		↑	↑	→	→				
					Rev.	Irrev.					
	20	↑		↑	↑	↑	→	→	→	→	→
							Rev.	Rev.	Rev.	Rev.	Rev.
5.3	5	↑			↑	↑	→	→	→		
							Rev.	Rev.	Rev.		
	10	↑			↑	↑	↑	↑	→	→	→
									Rev.	Rev.	Rev.

The symbols “↑” and “→” mean perpendicular and in-plane magnetic moments, respectively. The terms “Rev.” and “Irrev.” below the in-plane arrows mean that the Morin transition was found reversible and irreversible, respectively

structure with c-plane-oriented magnetic moments and dominates at higher temperatures [12]. In epitaxial films with the hexagonal (0001) growth, the c-axis-oriented magnetic moments correspond to perpendicular magnetic moments and the c-plane-oriented to in-plane magnetic moments. It is thought that the doped Ir has an effect to increase the single ionic magnetic anisotropy that favors c-axis-oriented magnetic moments and that results in the increase of Morin transition temperature, although the electronic mechanism has not been clearly understood yet. The hyperfine parameters, i.e., the isomer shift and the magnetic hyperfine field, do not change much after the Ir doping, so that the Fe environments do not seem electronically disturbed by the Ir doping. The Morin transition temperature on the other hand, decreases when the film thickness decreases. One of the possible mechanisms is a strain induced effect to the magnetic anisotropy, which is observed, for example, in ferromagnetic CoFe₂O₄(001) films [13, 14]. The tendency of the thickness dependence is, however, opposite to the reported tendency for very thin pure α-Fe₂O₃ layers deposited on Cr₂O₃ buffer layers on Al₂O₃ substrates, where the direction of the magnetic moments was examined using X-ray linear magnetic dichroism [15]. Note also that for the films prepared by a sputtering method, it seems that smaller amount of Ir results in a larger increase in the Morin transition temperature [9]. This is not so surprising because the Morin transition temperature is often very sensitive to the lattice imperfection and other sample status, which are linked with the sample preparation conditions [3, 11]. The origin of the irreversible phenomenon, which has been observed only for thin layers, is also unsolved. This may be

connected with an irreversible movement of constituent atoms, but there is no sign of a significant change in the Fe environments from the Fe Mössbauer spectra. At the present stage, no experimental information is obtained on the valence state of Ir, whether it is trivalent or tetravalent. If Ir is trivalent, the chemical formula should be $(\text{Fe}^{3+}_{1-x}\text{Ir}^{3+}_x)_2\text{O}_3$, whereas if tetravalent it should be $[(\text{Fe}^{3+}_{1-x}\text{Ir}^{4+}_x)_{3/(3+x)}V_{x/(3+x)}]_2\text{O}_3$ (V = vacancy), since ^{57}Fe is found trivalent from the Mössbauer analysis. This difference whether vacancies exist or not, would be important to achieve first principals calculations on the magnetic anisotropy of this system.

4 Summary

The Morin transition of very thin Ir-doped $\alpha\text{-Fe}_2\text{O}_3$ films, which is not detectable with conventional magnetization measurements, was studied by conversion electron Mössbauer spectroscopy using a ^{57}Co source and nuclear resonant scattering using a synchrotron light source. It was found that (i) the Morin transition temperature increases as the Ir ratio increases, (ii) it decrease when the film thickness decreases, and (iii) the transition becomes irreversible when Ir ratio is small and the thickness is thin. These tendencies were found systematic and reproducible, although the mechanisms are to be clarified by further studies.

Acknowledgments The authors would like to thank Dr. M. Sahashi, Dr. T. Nozaki, and Dr. T. Mitsui for fruitful discussion. The nuclear resonant scattering measurements were performed at BL09XU in SPring-8 (Proposal numbers 2016A0906, 2016B0906, and 2017A0906). These series of works were financially supported by IMPACT Program of Council for Science Technology, and Innovation from Cabinet Office, Japan, Grants-in-Aid for Scientific Research (B) (Grant number 25287086) and (S) (Grant number 24221005) from Japan Society for the Promotion of Science (JSPS) and MEXT, Japan, and a Grant-in-Aid from the Hori Sciences And Arts Foundation.

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