Temperature dependence of the hyperfine parameters on Fe$_3$O$_4$(111) surfaces

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Abstract

The Verwey transition on Fe$_3$O$_4$(111) surface was investigated using nuclear resonant x-ray scattering (NRS). Measurements were conducted below (85 K) and above (297 and 500 K) the Verwey transition temperature. The internal magnetic field estimated from the NRS frequency spectra agreed with that of bulk Fe$_3$O$_4$ at all measured temperatures. A clear change in the intensity ratio of the two peaks in the frequency spectra was observed across the Verwey transition. The results indicate that despite the presence of the peculiar surface electronic states which makes the changes in the electronic properties across the Verwey transition temperature blurred, the hyperfine parameters of the (111) surface show a clear change across the Verwey transition temperature.

1. Introduction

Magnetite (Fe$_3$O$_4$) is known as the oldest recognized magnetic material and has attracted interest due to its fascinating properties, such as half-metallicity [1], metal-to-semiconductor transition at $T_V = 122$ K called the Verwey transition [2, 3], and catalytic activity [4]. Above $T_V$, Fe$_3$O$_4$ crystallizes in a cubic inverse spinel structure (Fd$ar{3}$m). Its unit cell contains 24 Fe and 32 O ions. The 24 Fe sites consist of 8 tetrahedrally coordinated Fe(A) sites and 16 octahedral Fe(B) sites. The Fe(A) sites are occupied by Fe$^{3+}$ ions and the Fe(B) sites are occupied by an equal number of Fe$^{2+}$ and Fe$^{3+}$ ions. Fe$_3$O$_4$ is a ferrimagnet with the spins of the Fe(A) and the Fe(B) sites being anti-parallel to each other.

The surfaces of Fe$_3$O$_4$ have peculiar characteristics. The (100) surface has a superstructure with a band gap and a charge ordering up to 720 K [5], which resembles the bulk electronic structure below $T_V$ [6]. Due to the peculiar characteristic of the surface that resembles the bulk properties below $T_V$, the Verwey transition temperature appears to be much higher on the (100) surface than in the bulk [6]. A band gap has also been observed on the (111) surface at room temperature using scanning tunneling microscopy (STS) [7], which suggests that $T_V$ at the surface is higher than the room temperature. However, the details of the Verwey transition at the surface, particularly the (111) surface, are not fully understood.

To obtain insight into the influence of the surface on the Verwey transition, it is necessary to investigate the surface Verwey transition by a method other than detecting the change in the electronic structure. Bulk Verwey transition can be detected through changes in the electrical conductivity [2], lattice structure [8, 9], and hyperfine parameters [8, 10–12]. In this study, we implemented nuclear resonant x-ray scattering (NRS) measurement to investigate the change of hyperfine parameters across the Verwey transition on the Fe$_3$O$_4$(111) surface. Significant changes in the NRS frequency spectra between 297 and 85 K were observed, indicating that hyperfine parameters change significantly. The observed changes in the hyperfine parameters are consistent with the change of bulk Mössbauer spectra across the Verwey transition. This indicates that despite the large difference between the surface and the bulk electronic structure, the hyperfine parameters on the surface show changes similar to those of the bulk.

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2. Experiment

To enhance the signal intensity and the surface sensitivity, a 2 nm $^{57}$Fe$_3$O$_4$ epitaxial layer was deposited on a clean (111) surface of a natural Fe$_3$O$_4$ single crystal. The clean Fe$_3$O$_4$ (111) surface was prepared by sputtering with Ar$^+$ at 1 keV for 10 min at normal incidence, UHV annealing at 1000 K, and annealing at 1000 K under an oxygen pressure of $5 \times 10^{-4}$ Pa. The epitaxial $^{57}$Fe$_3$O$_4$ layer was grown by depositing $^{57}$Fe at a deposition rate of $\sim 0.01$ nm/s under an oxygen partial pressure of $5 \times 10^{-4}$ Pa. The 1 × 1 reflection high-energy electron diffraction pattern did not change after the $^{57}$Fe deposition, which indicates that the epitaxial $^{57}$Fe$_3$O$_4$ layer had grown on the surface [13]. The conversion electron Mössbauer spectrum taken after the deposition agreed well with the stoichiometric Fe$_3$O$_4$, which ensures the stoichiometry of the deposited layer [13].

The NRS measurements were carried out at the NE1 beam line of the High-Energy Accelerator Research Organization (KEK). The NRS spectra were taken at 85, 297, and 500 K. For the measurements at 297 and 85 K, which were conducted successively, the $^{57}$Fe$_3$O$_4$ (2 nm)/Fe$_3$O$_4$ (111) sample was transferred through the air to the UHV chamber, and cleaned by sputtering with Ar$^+$ at 1 keV for 10 min, UHV annealing at 900 K, and annealing at 900 K in an oxygen pressure of $5 \times 10^{-4}$ Pa. Because the sample obtained by this method has a low surface $^{57}$Fe density due to the loss of $^{57}$Fe during sputtering and annealing, it is not suitable for measurement in a high temperature region where the Lamb-Mössbauer factor is small [14] and the self diffusion of $^{57}$Fe is significant [15, 16]. Therefore, a sample cleaned by flashing at 750 K for 1 minute without sputtering after $^{57}$Fe$_3$O$_4$ deposition was used for the measurement at 500 K. The surface $^{57}$Fe nuclei were excited by linearly polarized synchrotron radiation (SR) of energy 14.413 keV, with glancing angles of 0.15–0.18°, which are confirmed to be in the total reflection regime by measuring the incidence angle dependence of reflectivity with a $\theta$–$2\theta$ geometry. The probing depth of NRS is typically a few nanometers in the total reflection regime, which is determined by the penetration depth of the incident x-ray [17]. The energy width of the SR was 6.5 meV and its magnetic field was vertical to the sample surface. The scattered beam was detected by avalanche photodiodes. The time spectra were obtained by accumulating the delay times of the delayed events. The counting rate of the delayed events was 0.039–0.085 s$^{-1}$, and 9402, 3070, and 10 351 delayed events were accumulated for the measurements at 85, 297, and 500 K, respectively. Each measurement took 17–59 h. During the measurement at 500 K, oxygen with a partial pressure of $1 \times 10^{-4}$ Pa was introduced in order to avoid desorption of oxygen. During the measurement, the time spectrum was monitored regularly. The shape of the time spectrum did not change significantly throughout the measurement, which verifies that the beam damage on the sample during the measurement is negligible. The measurements at 85 and 297 K were conducted under ultra-high vacuum with a base pressure lower than $1 \times 10^{-9}$ Pa.

3. Results and discussions

Figure 1(a) shows the time spectra of the nuclear resonant scattered x-ray taken at 85, 297, and 500 K. All the spectra exhibit clear quantum beats. Note that the intensity of the whole time spectra is different depending on the time. The frequency spectra were obtained through fast Fourier transformation (FFT). To minimize broadening of peaks in the frequency spectra due to the decay of the time spectra, the time spectra divided by exponential function $A \exp(-t/\tau)$ were used for FFT, where $A$ is a constant, $t$ is the time and $\tau$ is the decay time. $A$ and $\tau$ were obtained by curve fitting. The estimated $\tau$ were 54.7 ± 3.4, 54.3 ± 3.9, and 60.8 ± 4.8 ns for the time spectra at 85, 297, and 500 K, respectively. The deviation of $\tau$ from the life time of the first excited state of Fe nuclei (141 ns) is attributed to the speed-up effect due to the dynamical effect [18]. The speed-up effect weakens at high temperature where the Lamb-Mössbauer factor is small, which may account for the slight increase of $\tau$ at 500 K. The exponential curves are shown by dotted lines in figure 1(a). Figure 1(b) shows the frequency spectra. Because the intensity of the time spectra is weak in the $t > 250$ ns region, only the region $0$–$250$ ns was used for FFT. Here, Hanning window function was applied. We applied FFT by varying the position of the left edge of the time window from 0 to 5 ns and confirmed that the dependence of the frequency spectrum on the position of the time window was negligibly small.

In the frequency spectrum at 500 K, peaks were observed at 64 ± 2, 90 ± 4, 156 ± 2, and 166 ± 4 MHz. These shifted to higher frequencies upon cooling. The error bars of the frequency spectra and the uncertainty of the peak frequencies were estimated by performing FFT of 10 spectra with artificial shot noise. We have checked that the influence of the uncertainty of $\tau$ on the peak frequencies is negligibly small by dividing the time spectra with exponential function with various $\tau$ values and applying FFT. figure 2 shows the energy states of the $^{57}$Fe nucleus. The peaks at 156 ± 2 and 164 ± 4 MHz observed at 500 K in figure 1(b) are identified with the quantum beats originating from the interference of de-excitation lines $M = 3/2 \rightarrow 1/2$ and $M = -3/2 \rightarrow -1/2$ of the $^{57}$Fe nuclei, denoted by de-excitation lines 1 and 6, respectively, in figure 2, where $M$ is the magnetic quantum number [13]. Because Fe(A) has a larger internal magnetic field than Fe(B) above $T_V$, the peaks at 172 ± 2 and
Figure 1. (a) NRS time spectra of the $^{57}\text{Fe}_3\text{O}_4(2\ \text{nm})/\text{Fe}_3\text{O}_4(111)$ surface at 85 K, 297 K and 500 K. (b) Frequency spectra of the NRS time spectra of the $^{57}\text{Fe}_3\text{O}_4(2\ \text{nm})/\text{Fe}_3\text{O}_4(111)$ surface at 85 K, 297 K and 500 K. The arrows show the quantum beat frequencies $f_{13,46}$ and $f_{14,36}$, calculated using $B_{ij}$ estimated from the quantum beat frequencies of the interference between lines 1 and 6. The dashed and the solid arrows correspond to the Fe(B) and Fe(A) sites, respectively.

Figure 2. Energy states of $^{57}\text{Fe}$ nucleus in the excited $(l = 3/2)$ and ground states $(l = 1/2)$. 
Mössbauer spectra of Fe$_3$O$_4$ exhibit two sextets with different sizes of the Zeeman splitting. Above 500, 297, and 85 K, respectively. The intensities of the two peaks reversed between 297 and 85 K. This indicates the heights of the two peaks in the frequency spectrum of the intensities of the two sextets is 1.76 ± 2.20 [13], with the intensity of the sextet with smaller Zeeman splitting being larger than the other. Across $T_V$, these sextets reverse in intensity. [8] argued that the reversal in intensity is

184 ± 6 MHz at 297 K are assigned to Fe(B) and Fe(A), respectively. The peak at 90 ± 4 MHz observed at 500 K is considered to be the interference between the de-excitation lines 1 and 4, and 3 and 6, and the peak at 64 ± 2 MHz is assigned to the interference between lines 1 and 3, and 4 and 6. The peaks at 64 ± 2 and 90 ± 4 MHz consist of the contribution of Fe(A) and Fe(B) which have slightly different frequencies. However, the differences in their frequencies are too small to be resolved. The internal magnetic field strengths are estimated from the frequencies of the interference of the lines 1 and 6 by using the following equation,

$$B_{hf} = \hbar \cdot f / (\mu_{NNG} - 3\mu_{NGE}),$$  \hspace{1cm} (1)

where $f$ is the quantum beat frequency, $\mu_N$ is the nuclear magneton, $g_{NG}$ and $g_{NE}$ are the $g$ factor of the ground and the excited states, respectively, and $\hbar$ is the Planck constant. For $^{57}$Fe, $g_{NG} = 0.180$, and $g_{NE} = -0.103$ [19]. The results are shown in figure 3. The uncertainties of $B_{hf}$ are calculated from the uncertainties of the peak frequencies. The frequencies of the quantum beat of the interference between lines 1 and 3, and 4 and 6 ($f_{13,46}$) and lines 1 and 4, and 3 and 6 ($f_{14,36}$) calculated from the obtained $B_{hf}$ at 500 and 297 K are shown by arrows in figure 1(b). Here, we assumed that the quadrupole splitting is negligibly small [20]. The frequencies $f_{13,46}$ and $f_{14,36}$ agree well with the peak positions, verifying that our peak assignment is correct. The data shown by dotted lines in figure 3 are the internal magnetic fields of bulk Fe$_3$O$_4$ in the region 120–827 K taken from a previous study [21]. The origin of splitting of internal magnetic field of the Fe(B) sites observed in [21] is assumed to be due to the existence of two magnetically inequivalent Fe(B) sites [21]. These components are denoted as Fe(Ba) and Fe(Bb) in figure 3. The internal magnetic field strengths estimated from the quantum beat frequencies agreed with the bulk internal magnetic field strengths. Although data below 120 K is not available in [21], the estimated internal magnetic field components agreed well with the internal magnetic field strengths of the Fe(A) and Fe(B) sites at 297 and 500 K.

The agreement of the internal magnetic field strength calculated from the NRS frequency spectra with the bulk values indicates that the internal magnetic field is not influenced by the surface [6, 22, 23] within the experimental uncertainty. As described in the introduction, a previous STS study shows the presence of a band gap at the surface at room temperature. A change in the surface electronic structure is expected to have a strong influence on the internal magnetic field because it causes changes in the valence of Fe atoms [22]. However, such an effect was not observed in this study. This may indicate that the surface electronic structure is confined within a few atomic layers and that the internal magnetic field of the Fe atom probed by NRS, whose probing depth is typically ~2 nm, is almost uninfluenced by the surface electronic state. The ratio $I_1/I_3$, where $I_1$ and $I_3$ are the heights of the two peaks in the frequency spectrum (figure 1(b)) assigned to the interference between the lines 1 and 6 with $I_3$ corresponding to the peak at higher frequency, was 1.48 ± 0.14, 1.37 ± 0.32, and 0.640 ± 0.071 for 500, 297, and 85 K, respectively. The intensities of the two peaks reversed between 297 and 85 K. This indicates that hyperfine parameters change significantly across $T_V$.

Changes in the hyperfine parameters have been observed by Mössbauer spectroscopy [8, 10, 12, 24]. Mössbauer spectra of Fe$_3$O$_4$ exhibit two sextets with different sizes of the Zeeman splitting. Above $T_V$, the ratio of the intensities of the two sextets is 1.76–2.20 [13], with the intensity of the sextet with smaller Zeeman splitting being larger than the other. Across $T_V$, these sextets reverse in intensity. [8] argued that the reversal in intensity is
caused by the changes in the valence of Fe:
\[
[\text{Fe}^{3+}]_A[2\text{Fe}^{3+} + e^-]_B \rightarrow [\text{Fe}^{2+}]_A[\text{Fe}^{3+}]_B,
\]
which can be understood as the transition from the inverse-spinel to the normal-spinel structure. Senn et al.\cite{9} proposed another model to explain the mechanism of the Verwey transition. According to their model, Fe(B) is split into three components below \(T_V\), making it look as if the two sextets reverse in intensity\cite{11}. One of the most prominent differences between the two models is that the latter model includes a minor component with weak internal magnetic field and a large quadrupole splitting. This component is expected to appear as a peak at 135 MHz as can be estimated from the reported value of the internal magnetic field strength\cite{25}. However, this component accounts only for \(1/8\) of all Fe atoms, which is not large enough compared to the noise level in the frequency spectra shown in figure 1 (b). Therefore, at present, we are not able to determine which of the two models explains the experimental results of figure 1 (b) across \(T_V\) better. However, it is worth emphasizing that the reversal of the intensities of the two peaks originating from the interference between the de-excitation lines 1 and 6 is observed by NRS probing the shallow surface region, and is in good agreement with the reversal of the intensities of the two sextets in the Mössbauer spectrum across \(T_V\). This means that, despite the presence of the surface band gap which makes the changes in the electronic properties across \(T_V\) blurred at the surface\cite{7}, the change in hyperfine parameters on the (111) surface is clear. This may indicate that the surface electronic state is confined within the topmost layer and does not influence the NRS spectra whose probing depth is \(\sim 2\) nm, or that the surface band gap above \(T_V\) and the change in the hyperfine parameters are driven by different mechanisms, and are independent of each other.

4. Conclusions

In conclusion, the change of hyperfine parameters across the Verwey transition of Fe\(_3\)O\(_4\)(111) surfaces was investigated using NRS. The internal magnetic field of Fe sites at the Fe\(_3\)O\(_4\)(111) surface agrees with the bulk values within the experimental uncertainty. The change of intensity ratio of the two peaks in the NRS frequency spectra across \(T_V\) was observed, which is in good agreement with the change of bulk Mössbauer spectrum across \(T_V\), indicating that hyperfine parameters change significantly across the Verwey transition temperature.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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