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Magnetic structures of FeTiO3-Fe2O3 solid solution thin films studied by soft X-ray magnetic circular dichroism and ab initio multiplet calculations

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Magnetic structures of FeTiO₃-Fe₂O₃ solid solution thin films studied by soft X-ray magnetic circular dichroism and *ab initio* multiplet calculations

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The solid solutions between ilmenite (FeTiO₃) and hematite (α -Fe₂O₃) have recently attracted considerable attention as a spintronic material due to their interesting magnetic and electrical properties. In this study, the electronic and magnetic structures of epitaxially grown 0.6FeTiO₃·0.4Fe₂O₃ solid solution thin films were investigated by combining x-ray absorption near-edge structure (XANES), x-ray magnetic circular dichroism (XMCD) for two different crystallographic projections, and first-principles theoretical calculations. The Fe *L*-edge XANES and XMCD spectra reveal that Fe is in the mixed-valent Fe²⁺–Fe³⁺ states while Fe²⁺ ions are mainly responsible for the magnetization. Moreover, the experimental Fe *L*-edge XANES and XMCD spectra change depending on the incident x-ray directions, and the theoretical spectra explain such spectral features. We also find a large orbital magnetic moment, which can originate the magnetic anisotropy of this system. On the other hand, although the valence state of Ti was interpreted to be 4+ from the Ti *L*-edge XANES, XMCD signals indicate that some electrons are present in the Ti-3*d* orbital, which are coupled antiparallel to the magnetic moment of Fe²⁺ ions. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4868638]

Development of materials that show both magnetic and semiconducting properties is crucial for the realization of semiconductor-based spintronic devices. Equally important is to reveal the mechanism by which such properties arise. The solid solutions between ilmenite (FeTiO₃) and hematite $(\alpha$ -Fe₂O₃) have recently attracted considerable attention^{1-/} due to their interesting magnetic and electronic properties that are strongly dependent on ordering of cations as well as composition.^{8–13} Ferrimagnetic semiconductors arise when the arrangement of cations is ordered, whereas antiferromagnetism is observed for disordered cation distribution. The Curie temperature of ordered phases is higher than room temperature except for compositions more than about 80 mol. % of FeTiO₃. The p- and n-type semiconductors are reached for compositions greater and less than 73 mol. % of FeTiO₃, respectively. Also, spin-polarized carrier was theoretically predicted to be present for the solid solution.¹⁴

The emergence of both ferrimagnetism and electronic conduction in the solid solution has been qualitatively explained assuming a simple ionic model, where the nominal valence states of Fe ions and Ti ions in FeTiO₃ are +2 and +4, and that of Fe ions in Fe₂O₃ is +3. FeTiO₃ crystalizes in corundum-derivative structure, in which alternate (0001) layers of Fe²⁺ and Ti⁴⁺ ions are stacked along the *c*-axis. In the solid solution of FeTiO₃ with Fe₂O₃, it is generally assumed on the basis of electrostatic energy minimization

that Fe³⁺ ions are equally distributed between the layers, forming a charge ordered alternate (0001) layers of $(Fe^{2+} + Fe^{3+})$ and $(Ti^{4+} + Fe^{3+})$. As a result of antiferromagnetic interaction between neighboring (0001) layers, the magnetic moments of Fe³⁺ ions are canceled each other out, and only Fe²⁺ ions contribute to the magnetization. This assumption seems plausible from the compositional dependence of the saturation magnetization, however, there has been no direct experimental evidence except for one reported very recently using aberration-corrected scanning transmission electron microscopy coupled to high-energy-resolution electron energy-loss spectroscopy.¹⁵ Moreover, there have been several experimental data, including x-ray magnetic circular dichroism (XMCD),¹⁶ resonant x-ray photoemission spectroscopy,¹⁶ x-ray emission spectroscopy,^{17,18} and resonant inelastic x-ray scattering spectroscopy,¹⁹ which demonstrate that the Ti ions in FeTiO₃ intrinsically have some Ti³⁺ characters. These results suggest necessity to revisit the electronic and magnetic structures of FeTiO3-Fe2O3 solid solutions.

In this study, we have measured x-ray absorption nearedge structure (XANES) and XMCD spectra at the Ti $L_{2,3}$ and Fe $L_{2,3}$ -edges for 0.6FeTiO₃·0.4Fe₂O₃ solid solution thin films in order to clarify the electronic and magnetic structures of the compound. Using recently-developed first-principles configuration interaction (CI) method,^{20–22} it is now possible to predict XANES spectra of 3*d* transition metal compounds without any empirical parameters. XMCD spectra can also be calculated using the same method by taking

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the energy of external magnetic fields into the Hamiltonian. By comparing the experimental results with the first-principles theoretical spectra, we discuss the electronic and magnetic structures of the solid solution thin films. We have also performed the same set of experiments for $0.8\text{FeTiO}_3 \cdot 0.2\text{Fe}_2\text{O}_3$ thin film and got, essentially, the same results as those for $0.6\text{FeTiO}_3 \cdot 0.4\text{Fe}_2\text{O}_3$ thin film. Therefore, we believe that the findings of this work are the general phenomena of the FeTiO}_3 \cdot \text{Fe}_2\text{O}_3 solid solutions.

The thin film of 0.6FeTiO₃·0.4Fe₂O₃ solid solution with the ordered phase was epitaxially grown on an α -Al₂O₃(0001) substrate using a pulsed laser deposition method. The thin film was confirmed to be an *n*-type semiconductor and ferrimagnetic with the Curie temperature >400 K. Details of the sample fabrication and characterization are given in Ref. 2. In order to prevent surface deterioration, Au capping layer (~1.5 nm) was *in-situ* deposited after the thin film growth.

XANES and XMCD measurements were performed at soft x-ray beam line BL23SU²³ and BL25SU^{24,25} at SPring-8 in the total electron yield (TEY) mode using the photon beam with circular polarization rate of over 90%. XANES spectra (μ^+ , μ^-) were obtained using helicity switching of right-handed (μ^+) and left-handed (μ^-) circularly polarized x-rays under the applied magnetic field (*H*). XMCD spectra are given by the difference between μ^+ and μ^- . The photon *k* vector of the x-rays was set at 0° and 70° with respect to the normal line of the film surface for out-of-plane and in-plane measurements, respectively. Due to the presence of strong magnetic anisotropy with an easy axis in the direction parallel to the film surface, H = 10 T was applied to saturate the magnetization for the out-of-plane measurements, while H = 2 T was enough for the in-plane measurements.

Theoretical spectra at Fe and Ti $L_{2,3}$ -edges were calculated using a first-principles CI method.²⁰⁻²² We performed our calculations using model clusters composed of one transition metal ion and coordinating six oxide ions. The total number of electrons in the cluster was obtained from the formal charges. Possible valence states are +3 and +2 for Fe and +4 and +3 for Ti, respectively. Therefore, the clusters can be expressed as FeO_6^{9-} for Fe^{3+} , FeO_6^{10-} for Fe^{2+} , TiO_6^{8-} for Ti^{4+} , and TiO_6^{9-} for Ti^{3+} . Due to the difficulty in constructing a proper structure model for FeTiO₃-Fe₂O₃ solid solution, the atomic positions including the lattice constants were obtained from the experimentally reported values of FeTiO₃.²⁶ The photon k vector was set at parallel (k//c)and perpendicular $(k \perp c)$ to the trigonal c axis of the cation octahedra for the out-of-plane and in-plane calculations, respectively. For the XMCD calculation, a magnetic field of 10T was introduced parallel or antiparallel to the propagation direction of x-ray to induce the Zeeman splitting.

Figure 1 shows the Fe $L_{2,3}$ -edge XANES and XMCD spectra of 0.6FeTiO₃·0.4Fe₂O₃ solid solution thin films for two propagation directions of incident x-ray at 150 K. At the L_3 -edge, both XANES spectra are characterized by two peaks around 708.5 and 710 eV as shown in Figs. 1(a) and 1(b). Hereafter, we will call them peaks A and B, respectively. It is well known that Fe $L_{2,3}$ -edge XANES of Fe³⁺ in oxygen octahedron is typically characterized by two peaks around the transition energies of 708.5 and 710 eV, the latter



FIG. 1. Experimental (a) out-of-plane and (b) in-plane Fe $L_{2,3}$ -edge XANES spectra of 0.6FeTiO₃·0.4Fe₂O₃ solid solution thin films at 150 K. The corresponding XMCD spectra are shown in (c) and (d), respectively.

being the main peak. On the other hand, Fe^{2+} manifests only one peak around 708.5 eV.²⁷ The main peaks in experimental XMCD spectra are located at the transition energy of peak A, indicating that Fe^{2+} ions are mainly responsible for the magnetization of the solid solution. This result strongly supports the model of the solid solution that the magnetic moments of Fe³⁺ ions are canceled each other out and only Fe^{2+} ions contribute to the magnetization. This is the first direct experimental evidence for such a model. Note that unignorable contribution of Fe^{3+} ions to XMCD seems to be observed specially in the case of in-plane XMCD spectra. Spin canting between antiferromagnetic Fe³⁺ ions could be produced within the film plane. Comparing the in-plane and the out-of-plane XANES and XMCD spectra, we also notice that the fine structures are dependent on the incident directions: The A/B intensity ratios of XANES for the out-ofplane incidence are larger (~ 0.75) than those for the in-plane incidence (~ 0.72) [Figs. 1(a) and 1(b)], and the XMCD signals are broader for the in-plane incidence [Figs. 1(c) and 1(d)]. Incident-direction-dependence of XAENS and XMCD is in essence a linear dichroism effect which originates from the anisotropic spatial distribution of the Fe 3d electrons in a low-symmetry environment. Such an effect cannot be observed in bulk powder studies but is revealed due to the epitaxial nature of the samples.

In order to clarify the origin of the incident direction dependence of XANES and XMCD spectra, theoretical spectra were calculated. Figure 2 shows the calculated Fe $L_{2,3}$ -edge XANES and XMCD spectra of Fe^{2+} and Fe^{3+} in k//c and $k \perp c$ configurations. Hereafter, we assume that the main peaks of each spectra, which are around 708.5 eV for Fe^{2+} and 710 eV for Fe³⁺, correspond to the peak A and B, respectively. We find that the theoretical XANES and XMCD of Fe²⁺ [red lines in Fig. 2] show drastic incident-angle dependence compared with those of Fe^{3+} [black lines in Fig. 2]. This can be interpreted as the result of asymmetric distribution of 3*d* electrons in Fe²⁺ (d^6) compared to the symmetric distribu-tion in Fe³⁺ (d^5). As seen from Figs. 2(a) and 2(b), at the L_3 -edge, Fe²⁺ in the k//c configuration mainly contributes to peak A of the XANES spectrum while Fe^{2+} in the $k \perp c$ configuration is characterized by two peaks: One contributes to the peak A, and the other lies between the peak A and B.



FIG. 2. Theoretical (a) out-of-plane and (b) in-plane Fe $L_{2,3}$ -edge XANES spectra of Fe²⁺ and Fe³⁺ in FeTiO3 at 150 K. The corresponding XMCD spectra are shown in (c) and (d) for Fe²⁺ and (e) and (f) for Fe³⁺.

The theoretical XMCD spectrum of Fe²⁺ in the $k \perp c$ configuration [Fig. 2(d)] also manifests two peaks at the L_3 -edge. This can be the reason the experimental in-plane XMCD gives broader signals; the broader spectrum obtained experimentally can be decomposed into two peaks as suggested theoretically. A closer look at the XANES of Fe²⁺ reveals that the intensity of peak A, that is the average of μ^+ and μ^- , is higher for the k//c configuration than that for the $k \perp c$ configuration. Therefore, the most probable interpretation of the incident-angle dependence of the experimental XANES should be the contribution of Fe²⁺.

We have applied the XMCD sum rules^{28–30} to the experimental results in order to estimate the ratio of orbital to spin magnetic moment m_{orb}/m_{spin} for each of the incident directions, which can be expressed as

$$\frac{m_{orb}}{m_{spin} + 7\langle T_z \rangle} = \frac{2}{3} \times \frac{\int_{L_{2,3}} (\mu_+ - \mu_-) d\omega}{\int_{L_3} (\mu_+ - \mu_-) d\omega - 2 \int_{L_2} (\mu_+ - \mu_-) d\omega},$$
(1)

where $\langle T_z \rangle$ is the expectation value of magnetic dipole operator. This equation requires no information on the background of XANES, the average number of 3*d* holes, and the degree of circular polarization of incident photons. The $m_{\rm orb}/(m_{\rm spin} + 7\langle T_z \rangle)$ ratios are 0.21 and 0.14 for in-plane and out-of-plane directions, respectively, and larger contribution of orbital moment was found for the in-plane incidence. We also calculated the $m_{\rm orb}/(m_{\rm spin} + 7\langle T_z \rangle)$ ratios for the theoretical spectra and obtained a consistent result. Assuming uniaxial anisotropy, the magnitude of $\langle T_z \rangle$ was estimated to be $-0.0016 \,\mu_{\rm B}$ and $0.0008 \,\mu_{\rm B}$ for the out-of-plane and in-plane directions, respectively, which should be much smaller than $m_{\rm spin}$. The presence of larger $m_{\rm orb}$ for in-plane direction can be the origin of the strong magnetic anisotropy observed in this system.^{2,4} Note that XANES recorded with the TEY mode typically suffers from the saturation effect, leading to an underestimation of the orbital moments.³¹ However, this does not affect our conclusion because the underestimation of orbital moment is more significant for the in-plane incidence. Moreover, the values of the $m_{\rm orb}/(m_{\rm spin} + 7\langle T_z \rangle)$ ratios themselves are rather large (0.21 for in-plane direction) although the orbital moment is generally quenched by the crystal field in transition metal oxides. Namely, no small contribution of $m_{\rm orb}$ to the total magnetization is expected in this material. Some of the previous experimental data on the magnetization can be explained as the contribution of $m_{\rm orb}$. One example is the saturation magnetization observed for bulk polycrystalline FeTiO₃-Fe₂O₃ solid solution. The value of saturation magnetization of the solid solution is reported to be $4 \mu_{\rm B}/{\rm Fe}^{2+.32}$ At a glance, this is a reasonable value theoretically expected from the spin-only contribution. Nonetheless, considering the presence of strong magnetic anisotropy in the crystal and the fact that grains with an easy and hard axis are randomly distributed, the value of the saturation magnetization should be smaller if only spins contribute to the magnetization. Hence, it is suggested that the orbital as well as the spin contributes to the above-mentioned value of saturation magnetization. Second example is on the epitaxial thin film of the solid solution. We reported that the saturation magnetization of the 0.63FeTiO₃·0.37Fe₂O₃ epitaxial thin film is about $3 \mu_{\rm B}$ /f.u. along the axis of easy magnetization,² although the spin-only magnetization expected for that composition is $2.52 \,\mu_{\rm B}$ /f.u. (4 multiplied by 0.63).

Figure 3 shows the Ti $L_{2,3}$ -edge XANES and XMCD spectra of 0.6FeTiO₃·0.4Fe₂O₃ solid solution thin films for two directions of incident x-ray at 150 K. As shown in Figs. 3(a) and 3(b), the experimental Ti $L_{2,3}$ -edge XANES spectra manifest little incident angle dependence unlike the case of Fe. The experimental XANES spectrum consists of four peaks, which arise from the spin-orbit splitting of the Ti 2p level as well as the crystal-field splitting of the Ti 3d level. This kind of spectrum has been interpreted to be Ti⁴⁺ in oxygen octahedron.³ Surprisingly, however, there exists undeniable XMCD signal as seen from Figs. 3(c) and 3(d). One can also notice that the XMCD spectra exhibit incident-direction dependence. The fine structure of the in-plane XMCD is very similar to that observed for bulk crystal of FeTiO₃.¹⁶ In Fig. 3(e), we show the in-plane Ti L2.3-edge XMCD hysteresis loop for 0.6FeTiO₃·0.4Fe₂O₃ at 300 K. In order to eliminate the non-magnetic background, magnetic field dependence of the XMCD intensity was measured at the photon energy of 464.5 and 466 eV, and the difference between them is used for the hysteresis loop.³⁵ Figure 3(e) also illustrates the magnetic field dependence of magnetization measured with a superconducting quantum interference device magnetometer.² The shape of the hysteresis loop is essentially the same as that of the magnetization. Therefore, the XMCD signals are not due to any experimental artifacts but suggest that the Ti ions in the solid solution thin films intrinsically have magnetically polarized 3d electrons. Note that the sign of the XMCD hysteresis loop is arbitrary, and we cannot tell if the magnetic moment of Ti is parallel or anti-parallel to the magnetic field only from the experimental results.

To get an insight into the nature of Ti 3d electrons, theoretical Ti $L_{2,3}$ -edge XANES and XMCD spectra were



FIG. 3. Experimental (a) out-of-plane and (b) in-plane Ti $L_{2,3}$ -edge XANES spectra of 0.6FeTiO₃·0.4Fe₂O₃ at 150 K. The corresponding XMCD spectra are shown in (c) and (d). (e) In-plane Ti $L_{2,3}$ -edge XMCD hysteresis loop of 0.6FeTiO₃·0.4Fe₂O₃ at 300 K (closed circles). The photon energies used for the XMCD hysteresis loop are indicated by arrows in the (d). Magnetic field dependence of in-plane magnetization of 0.6FeTiO₃·0.4Fe₂O₃ at 300 K (Ref. 2) is also shown for comparison (open circles).

derived for both k//c and k \perp c configurations assuming Ti⁴⁺ (d^0) and Ti³⁺ (d^1) states. The results are shown in Fig. 4. The calculated XANES spectra of Ti⁴⁺ [black lines in Figs. 4(a) and 4(b)] agree well with the experimental ones. On the other hand, the experimental Ti- $L_{2,3}$ XMCD signals can be better explained if we assume the presence of Ti³⁺ that is coupled antiparallel rather than parallel with the magnetic field [red lines in Figs. 4(c) and 4(d)]. These results suggest the presence of Ti³⁺ in the solid solution and their contribution to the XMCD spectra. The Fe²⁺ \rightarrow Ti⁴⁺ charge transfer caused by the Fe 3*d*-Ti 3*d* hybridization is generally



FIG. 4. Theoretical (a) out-of-plane and (b) in-plane Ti $L_{2,3}$ -edge XANES spectra of Ti⁴⁺ and Ti³⁺ in FeTiO₃ at 150 K. The corresponding XMCD spectra are shown in (c) and (d), respectively.

proposed as the origin of Ti^{3+} in FeTiO₃. Although the transfer mechanism is still controversial, ^{19,36–38} theoretical calculations suggest that the Fe 3d minority-spin orbital hybridizes with the Ti 3d orbital.^{36,39} Interestingly, this picture is consistent with our finding that Ti³⁺ is coupled antiparallel with the magnetic field. It should be noted that not only Ti³⁺ but also Ti⁴⁺ give finite XMCD signal, even though Ti^{4+} with $(3d)^0$ configuration does not have magnetic moment at the ground state. The Ti⁴⁺ XMCD signals are enhanced by applying larger magnetic fields (not shown): These results indicate that the Ti⁴⁺ XMCD signals originate from the magnetic polarization at the final states of $Ti-L_{2,3}$ XANES with $(2p)^5(3d)^1$ configuration. However, the fine structures appearing in the experimental Ti-L2,3 XMCD spectra cannot be explained only by the Ti⁴⁺ contribution. Further systematic experiments should be carried out to explore the origin and the nature of the electron in Ti 3d orbital.

In conclusion, we have investigated the electronic and magnetic structures of epitaxially grown FeTiO₃-Fe₂O₃ solid solution thin films by combining XANES, XMCD for two different crystallographic projections, and first-principles theoretical calculations. The Fe L-edge XANES and XMCD spectra reveal that Fe is in the mixed-valent Fe²⁺-Fe³⁺ states while Fe²⁺ ions are mainly responsible for the magnetization of the solid solution. It is also demonstrated that the first-principles calculation in combination with the angle resolved XANES and XMCD spectra is a powerful tool to study the anisotropy of Fe 3d electrons in the solid solution. Applying XMCD sum rule, we find a large orbital magnetic moment with anisotropy, which can be the origin of magnetic anisotropy. On the other hand, although the valence state of Ti was interpreted to be 4+ from the Ti $L_{2,3}$ -edge XANES, XMCD signals indicate that some electrons are present in the Ti-3d orbital, which are coupled antiparallel to the magnetic moment of Fe^{2+} ions.

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