Electronic structure and magnetic properties of Al-doped Fe₃O₄ films studied by x-ray absorption and magnetic circular dichroism

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The electronic structure and magnetic properties of Al-doped Fe₃O₄ films at various Al concentrations were investigated by Al and O *K*-edge x-ray absorption near-edge structure (XANES) and Fe *L*_{3,2}-edge magnetic circular dichroism (MCD) measurements. The O *K*-edge XANES spectra reveal that the intensity of O 2*p*-Fe 3*d* hybridized states decreases linearly as the Al concentration increases, suggesting that nonmagnetic Al substitution reduces couplings of the O 2*p* with Fe 3*d* orbitals. The Fe *L*₃-edge MCD spectra show that the intensities of MCD features decrease as the Al concentration increases, which suggests that Al substitution reduces the magnetic moments of Fe ions. The Fe *L*_{3,2} XANES spectra suggest the absence of mixed valence states in agreement with previous x-ray resonance scattering measurements. © 2005 American Institute of Physics. [DOI: 10.1063/1.1863450]

Magnetite (Fe₃O₄) has been regarded as a mixed-valence 3*d* transition-metal compound and has attracted much interest because of its potential applications in magnetic devices and future spintronics.¹ The valence states of Fe ions in Fe₃O₄ have usually been assigned according to the chemical formula, (Fe³⁺)_A[Fe²⁺Fe³⁺]_BO₄, where the parentheses and brackets refer to tetrahedral A- and octahedral B-sites, respectively. The magnetic moments of Fe³⁺ ions on tetrahedral A-sites, Fe³⁺(A), and octahedral B-sites, Fe³⁺(B), have been assigned to have the same magnitude but in opposite direction, so that they cancel out. Thus the net magnetic moment of Fe₃O₄ is due to ferromagnetic arrangement of Fe²⁺ ions on B-sites, Fe²⁺(B).² The presence of Fe²⁺ and Fe³⁺ ions on the octahedral B-sites was argued to result in high electrical conductivity at room temperature because carriers hop between Fe²⁺(B) and Fe³⁺(B) ions.³ However, García *et al.*^{4,5} recently showed the absence of mixed Fe²⁺(B) and Fe³⁺(B) ions using x-ray resonance scattering measurements. As the temperature is reduced, the electrical conductivity drops abruptly by two orders of magnitude at about 120 K accompanied by a decrease of the magnetic moment. This peculiar first-order metal-insulator phase transition is known as the Verwey transition.⁶ The partial substitution of Fe ions with magnetic⁷ and nonmagnetic⁸ metallic ions can alter the electronic structure and magnetic property of the magnetite. However, the partial substitution of either Fe²⁺ and/or Fe³⁺ and A- and/or B-sites in the spinel structured Fe₃O₄ remains to be controversial.⁹⁻¹² In this work, x-ray absorption near-

edge structure (XANES) and magnetic circular dichroism (MCD) measurements were made to elucidate the effect of Al substitution on the electronic structure and magnetic property of Fe₃O₄.

The O and Al *K*-edge XANES and Fe *L*_{3,2}-edge MCD were obtained using a high-energy spherical grating monochromator and Dragon beamlines, respectively, by the fluorescence and electron yield modes at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The x-ray MCD measurement was made by applying an alternating magnetic field of 1×10^4 Oe parallel to the surface of the sample, and the grazing angle of the incident light was fixed at 30° from the sample's surface. Al_{*x*}-(Fe₃O₄)_{1-*x*} (*x*=0, 0.01, 0.05, and 0.1) composite films, defined as Al(*x*)-doped Fe₃O₄, were used in this work and were prepared by dc magnetron sputtering technique on thermally oxidized silicon (100) wafers with the composite targets made from Fe₃O₄ and Al powder at temperature of 350 °C and a pressure of 5×10^{-3} Torr. The single-phase Al(*x*)-doped Fe₃O₄ films were characterized by x-ray diffraction. The preparation of the samples is detailed elsewhere.¹³

Figure 1 presents the Al *K*-edge XANES spectra of various Al(*x*)-doped Fe₃O₄ (*x*=0, 0.01, 0.05, and 0.1) compounds and the pure Al metal. The spectra are normalized to the incident beam intensity, *I*₀, with the area under the spectra in the energy range between 1632 and 1636 eV fixed. The general line shapes of the Al *K*-edge XANES spectra of the various Al(*x*)-doped Fe₃O₄ are very similar but differ significantly from that of pure Al. The intensities of the leading features of these Al(*x*)-doped Fe₃O₄ compounds are significantly enhanced and the inflection point of the threshold

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FIG. 1. Al K -edge XANES spectra of various Al(x)-doped Fe_3O_4 ($x=0, 0.01, 0.05$, and 0.1) compounds and pure Al metal. The inset presents the magnified leading features.

clearly shift to the higher energy relative to that of pure Al. According to the dipole-transition selection rules, the leading feature in Fig. 1 is due to transitions from $1s$ core state to unoccupied Al $3p$ -derived states, which hybridize strongly with O $2p$ states in the Al(x)-doped Fe_3O_4 . The inset in Fig. 1 shows that the leading feature shifts to higher energy as indicated by the arrow, while the intensity of the leading feature decreases, when x is increased from 0.01 to 0.1 for Al(x)-doped Fe_3O_4 samples. This result suggests that Al loses more p -orbital charge to the Fe_3O_4 host and has a more attractive electrostatic potential when the Al concentration is lower.¹⁴

Figure 2 presents the normalized O K -edge XANES spectra of the various Al(x)-doped and pure Fe_3O_4 films. The O K -edge XANES spectra reflect transitions to oxygen unoccupied $2p$ -derived states. Features *a* and *b* are primarily unoccupied hybridized states between relatively narrow $3d$ and broader $4sp$ bands of Fe ions, respectively. The inset in Fig. 2 displays magnified feature *a* for various Al concentrations after the subtraction of the background represented by a best-fitted Gaussian curve (dashed line). Feature *a* is a two-peak feature just above the threshold, which can be assigned as a mixture of e_g and t_{2g} states. Similar two-peak O K -edge threshold feature was also found for $3d$ -transition-metal oxides.^{15,16} The intensity of feature *a* decreases as the Al concentration x increases, which suggests that nonmagnetic Al substitution reduces couplings between O $2p$ and Fe $3d$ orbitals in the Al(x)-doped Fe_3O_4 because Al substitution reduces the number of available Fe $3d$ states that can couple to O $2p$ states.

Figure 3 shows the normalized Fe $L_{3,2}$ -edge XANES and MCD (i.e., $I_+ - I_-$) spectra of various Al(x)-doped and pure Fe_3O_4 films. $I_+(I_-)$ refers to the absorption spectrum obtained by projecting the spin of the incident photons parallel (anti-parallel) to the direction of the Fe $3d$ majority spin. The general line shapes of the Fe $L_{3,2}$ -edge XANES and MCD

FIG. 2. Normalized O K -edge XANES spectra of various Al(x)-doped and pure Fe_3O_4 compounds. The inset presents magnified near-edge features after background subtraction.

spectra of the various Al(x)-doped and pure Fe_3O_4 films are similar to those of Fe_3O_4 reported previously.^{17,18} Figure 4 presents a magnified view of the MCD features at the Fe L_3 -edge, which contains two prominent negative and one positive (~ 709.6 eV) MCD features. Kuiper *et al.*¹⁷ and Chen *et al.*¹⁸ attributed the two negative features to the Fe ions at the octahedral B-sites, $\text{Fe}^{2+}(\text{B})$ and $\text{Fe}^{3+}(\text{B})$, and the positive feature to the Fe ions at the tetrahedral A sites, $\text{Fe}^{3+}(\text{A})$. The inset in Fig. 4 plots the integrals of the two negative features from 703.3 to 709.4 eV (indicated as B_1) and from 709.8 to 711.6 eV (B_2), respectively, and the positive feature from 709.4 to 709.8 eV(A) in the Fe L_3 -edge MCD spectra as functions of Al. The inset shows that the

FIG. 3. Normalized Fe $L_{3,2}$ -edge XANES and MCD spectra of various Al(x)-doped and pure Fe_3O_4 compounds.

FIG. 4. Magnified view of MCD features at the Fe $L_{3,2}$ -edge. The inset presents the integrals of the two negative and one positive features in Fe $L_{3,2}$ -edge MCD spectra as functions of x .

intensities of negative MCD features decrease significantly and the intensity of the positive MCD feature decreases slightly as the Al concentration increases, which suggest that Al substitution reduces the overall magnetic moment of Fe ions.

The similar decrease of both intensities of negative features, which were interpreted as due to $\text{Fe}^{2+}(\text{B})$ and $\text{Fe}^{3+}(\text{B})$ ions, suggest substitution of Fe^{2+} ions by Al ions with a valence of +3. In this case Al atoms are donors or deep traps and the electronic structure, especially the conduction band, will be greatly altered and depends strongly on the concentration of Al, which seems not consistent with the observed Al and O K -edge and Fe $L_{3,2}$ -edge XANES spectra. Recently, García *et al.*^{4,5} found absence of Fe^{2+} and Fe^{3+} charge ordering in Fe_3O_4 . They found that Fe_3O_4 is not a fluctuating mixed valence material. To reconcile this finding, we have proposed an alternative interpretation of Fe $L_{3,2}$ -edge MCD features. The Fe $L_{3,2}$ -edge XANES and MCD spectra contain contributions from B-site Fe ions with spins polarized in one direction and A-site Fe ions with spins polarized in the opposite direction. The two negative MCD features shown in Fig. 3 and magnified in Fig. 4 have a separation of about 2 eV, which is close to that of the twin-peak feature *a* in the O K -edge XANES spectra. Thus these two negative MCD features reflect spin polarized Fe $3d\ e_g$ and t_{2g} bands. The intensities of these two features are the difference intensities between the contributions from the 2/3 Fe ions on the B-site and from the 1/3 Fe ions on the A-site. The positive MCD feature between these two negative features actually is the part of the contribution from the 1/3 Fe ions on the A-site, which is not overshadowed by the negative contribution from those Fe ions on the B-site.

The mixed valence picture of Fe_3O_4 is based on an assumption that this material is 100% ionic and the effective charges of Fe ions can be determined by numbers of neighboring O ions, so that B-site Fe ions were assigned with +2 and +3 charge states and A-site Fe ions were assigned with

the +3 charge state. However, Fe has an electronegativity of 1.83,¹⁹ which is significantly larger than those of alkali and alkaline earth metals. Besides, $3d$ electrons of Fe are not as easy as $4sp$ electrons to be ionized. Thus, Fe_3O_4 is not 100% ionic. If +2 and +3 charge states coexist, the on-site electrostatic potential seen by an electron at Fe^{3+} will be more attractive than that at Fe^{2+} by $\Delta V \approx -e^2/(R)$, where R is an effective radius of the $3d$ orbital, without the screening effect of conduction electrons: $\Delta V \approx 8$ eV for $R \approx 1.2$ Å. Both $2p$ core and unoccupied $3d$ states see this extra attractive potential. However, since unoccupied $3d$ states extend outside the Fe ion, the average extra attractive potential seen by unoccupied $3d$ states is smaller than that of $2p$ core states, which are localized inside the Fe ion. Thus, the $L_{3,2}$ -edge XANES features, which reflect the energy difference between unoccupied $3d$ states and $2p$ core states will shift to higher energy relative to that of Fe^{2+} , so that Fe $L_{3,2}$ XANES spectra will show two sets of L_3 and L_2 features. However, only a single set of L_3 and L_2 features are observed as shown in Fig. 3. The Fe K -edge XANES spectrum of Fe^{3+} in the compounds has generally been observed to shift to higher energy side relative to that of Fe^{2+} . However, we do not see any considerable energy shift in our Fe K -edge XANES measurements of Al(x)-doped Fe_3O_4 (not shown). Thus, our XANES measurements show the absence of mixed valence states in agreement with x-ray resonance scattering measurements of García *et al.*^{4,5}

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