Electronic and magnetic properties of the Ag-doped Fe$_3$O$_4$ films studied by x-ray absorption spectroscopy

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The electronic and magnetic properties of Ag-doped Fe$_3$O$_4$ films were studied by x-ray absorption near-edge structure (XANES), extended x-ray absorption fine structure (EXAFS), and x-ray magnetic circular dichroism (XMCD) measurements. A comparison between the Ag K-edge EXAFS Fourier transform spectra of Ag-doped Fe$_3$O$_4$ and the Ag metal shows that Ag atoms aggregate into Ag granules. The O K-edge and Ag L$_3$-edge XANES spectra consistently indicate an electron transfer from the Fe$_3$O$_4$ host into Ag granules. The Fe L$_{3,2}$-edge XMCD spectra and hysteresis measurements reveal that Ag granules reduce the average magnetic moment of Fe ions and the saturation magnetization of Fe$_3$O$_4$.

Magnetite (Fe$_3$O$_4$) is a well-known compound, which exhibits a first-order metal-insulator phase transition called the Verwey transition. The valence states of Fe ions in the inverse-spinel-structured Fe$_3$O$_4$ have typically been assigned according to the chemical formula, (Fe$_{3+}$)$_{0.5}$Fe$_{2+}$Fe$_{3+}$O$_4$, where the parentheses and square brackets refer to tetrahedral A and octahedral B sites, respectively. Recently Versluijs et al. and Chung et al. explained the magnetoresistive effect of Fe$_3$O$_4$ by the hopping transport of spin-polarized electrons through a narrow domain wall pinned at the nanocontacts. Magnetite is a potential candidate for spintronics materials. Hsu et al. observed an anomalous magnetoresistance in Ag-doped Fe$_3$O$_4$ composite films and interpreted this finding as being caused by magnetic-field induced spin injection from Fe$_3$O$_4$ into Ag granules, which impedes the current. Partial substitution of Fe ions with magnetic and nonmagnetic metallic ions was also found to change the electronic and magnetic properties of Fe$_3$O$_4$. Al-doped Fe$_3$O$_4$ composite films have been investigated by Yang et al. using x-ray absorption near-edge structure (XANES) and x-ray magnetic circular dichroism (XMCD) measurements. Since Ag differs from Al by having shallow 4$d$ states, which may affect the magnetic properties of Fe$_3$O$_4$ and Ag was argued to form granules in Fe$_3$O$_4$, it is interesting to use x-ray spectroscopy to understand the electronic and magnetic properties of Ag-doped Fe$_3$O$_4$ composite films.

The O K- and Ag L$_3$-edge XANES, Ag K-edge extended x-ray absorption fine structure (EXAFS), and Fe L$_{3,2}$-edge XMCD were obtained using a high-energy spherical grating monochromator-20A, BL-15B, superconducting wavelength shifter-01C and Dragon-11A beamlines, respectively, at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Ag$_x$-(Fe$_3$O$_4$)$_{1-x}$ (x=0, 0.05, and 0.1) composite films, denoted by Ag(x)–Fe$_3$O$_4$, were prepared by dc magnetron sputtering on thermally oxidized silicon (100) wafers with the composite targets made from Fe$_3$O$_4$ and Ag powder at a temperature of 350 °C. The preparation and characterization of the samples have been described elsewhere.

Figure 1 presents the Fourier transform (FT) amplitudes of the EXAFS $k^3\chi$ data at the Ag K-edge for the Ag(x)–Fe$_3$O$_4$ films, the reference Ag metal, and AgO powder. The inset displays Ag K-edge EXAFS oscillations $k^3\chi$ data. The similarity between the FT spectra of the Ag(x)–Fe$_3$O$_4$ films and the Ag metal indicates that the local atomic environment of Ag atoms in Ag(x)–Fe$_3$O$_4$ films is similar to that in the Ag metal, but differ drastically from that in AgO. The first dominant peak in the FT spectra of the Ag K-edge EXAFS $k^3\chi$ data from $k=3.3$ to 12.5 Å$^{-1}$ for the Ag(x)–Fe$_3$O$_4$ films and the reference Ag metal and AgO powder. The inset plots the corresponding Ag K-edge EXAFS oscillations $k^3\chi$ data.
Ag($\chi$)--Fe$_3$O$_4$ and the Ag metal is attributed to the nearest-neighbor Ag--Ag bond length (i.e., radial distance) of ~2.89 Å. The same Ag--Ag bond lengths in the spectra of Ag($\chi$)--Fe$_3$O$_4$ and the Ag metal strongly suggests that Ag atoms aggregate into Ag granules in the Ag($\chi$)--Fe$_3$O$_4$ films. The distinctly different Ag--Ag bond lengths in Ag($\chi$)--Fe$_3$O$_4$ and AgO show no evidence of Fe ions partially substituting by Ag ions and in fact that Ag granules are dominantly in contact with Fe ions instead of O ions. Additional Fe K-edge EXAFS measurements for Ag($\chi$)--Fe$_3$O$_4$ (not shown) show that the local atomic environment of the Fe atoms in the Ag($\chi$)--Fe$_3$O$_4$ ($\chi=0.05$ and 0.1) films closely resembles that of the Fe$_3$O$_4$ ($\chi=0$) sample, which indicates that addition of Ag does not change the inverse spinel structure of the Fe$_3$O$_4$ composite films.

Figure 2 shows the normalized Ag L$_3$-edge XANES spectra of the Ag($\chi$)--Fe$_3$O$_4$ films, Ag metal, and AgO powder. According to the dipole-transition selection rule, the Ag L$_3$-edge XANES spectra predominantly reflect transitions from the Ag 2p core level to unoccupied Ag 4d/5s-derived states. As shown in Fig. 2, the spectral features of the Ag($\chi$)--Fe$_3$O$_4$ films closely resemble those of the Ag metal but differ clearly from those of AgO; in particular, the near-edge features of the Ag($\chi$)--Fe$_3$O$_4$ films and the Ag metal (Ag$^{3+}$) lie much higher energy than that of AgO (Ag$^{2+}$), which agrees with earlier observation by Kolobov et al. The result of the formation of metallic Ag granules and the absence of the Ag--O bonding in the Ag($\chi$)--Fe$_3$O$_4$ films is consistent with the Ag K-edge EXAFS observation. The bottom of Fig. 2 displays the difference Ag L$_3$-edge near-edge spectrum between the Ag($\chi$)--Fe$_3$O$_4$ and the Ag metal, which shows reduction of the density of unoccupied Ag 4d/5s states in Ag($\chi$)--Fe$_3$O$_4$. This result suggests an electron transfer from the Fe$_3$O$_4$ host into the Ag granules. The direction of charge transfer suggests that at the Fe$_3$O$_4$/Ag granule interfaces, the interface dipoles point towards the Ag granule, as a result that the electrostatic potential in the Ag granule is lowered relative to that in the Fe$_3$O$_4$ host. The direction of dipoles implies that Ag atoms at the interfaces are dominantly in contact with Fe ions, which have positive effective charges. This argument is consistent with the observation of the absence of AgO by EXAFS measurement.

Figure 3 displays the normalized O K-edge XANES spectra of the Ag($\chi$)--Fe$_3$O$_4$ films. The O K-edge XANES spectra reflect transitions to unoccupied 2p-derived states of oxygen and the states of neighboring ions, which have significant p-symmetry components projected onto the O sites and usually hybridize with O 2p states. Features a and b are mainly unoccupied hybridized states between O 2p and relatively narrow 3d and broader 4sp bands of Fe ions, respectively. The inset in Fig. 3 magnifies feature a for the Ag($\chi$)--Fe$_3$O$_4$ films after the background represented by a best-fitted Gaussian curve (dashed line) has been subtracted. The intensity of feature a increases slightly with the Ag concentration $\chi$, which indicates that Ag increases slightly the unoccupied O 2p-Fe 3d states in Ag($\chi$)--Fe$_3$O$_4$. This trend is opposite to that of Al($\chi$)--Fe$_3$O$_4$, for which the intensity of feature a decreases as the Al concentration $\chi$ increases. Figure 4(a) presents the normalized Fe L$_{3,2}$-edge XANES and XMCD (i.e., $I_+ I_-$) spectra of the Ag($\chi$)--Fe$_3$O$_4$ films. $I_+ (I_-)$ refers to the absorption spectrum obtained by projecting the spin of the incident photons parallel (antiparallel) to the direction of the Fe 3d majority spin. The general line shapes of the Fe L$_{3,2}$-edge XANES and XMCD spectra of these Ag($\chi$)--Fe$_3$O$_4$ films are similar to those of Fe$_3$O$_4$ reported elsewhere. Figure 4(b) displays a magnified view of the XMCD features at the Fe L$_1$ edge, which shows two prominent negative and one positive XMCD features.
Whether Fe ions have Fe$^{2+}$ and Fe$^{3+}$ charge orderings or a fluctuating mixed valence state in the inverse-spinel-structured Fe$_3$O$_4$ remains controversial.\textsuperscript{18,19} Kuiper \textit{et al.} based on the Fe$^{2+}$ and Fe$^{3+}$ charge orderings attributed the two negative features to the Fe ions at the octahedral $B$ sites, namely, Fe$^{2+}$(B) and Fe$^{3+}$(B), and the positive feature to the Fe ions at the tetrahedral $A$ sites, Fe$^{3+}$(A).\textsuperscript{14} On the other hand, Yang \textit{et al.}\textsuperscript{10} attributed the two negative XMCD features, which have a separation of approximately 2 eV in close agreement with that of the twin-peak feature A in the $O$ K-edge XANES spectra, to the spin-polarized Fe 3$d_{eg}$ and $t_{2g}$ bands of $B$ site Fe ions and the positive XMCD feature in between to the remnant intensity of the 3$d_{eg}$ states of the $A$-site Fe ions, which is not overshadowed by the two negative features. Figure 4(b) demonstrates that the intensities of the XMCD features decrease significantly as the Ag concentration increases, which indicates that the embedding of Ag granules in Fe$_3$O$_4$ reduces the overall magnetic moment of Fe ions. The interpretation of the decrease of the XMCD intensity as a reduction of the overall magnetic moment of the Fe ions is confirmed by the magnetic hysteresis measurements of Ag(x)–Fe$_3$O$_4$ shown in the inset of Fig. 4(b) and the magnetic force microscopic measurement (not shown). The hysteresis loops show that the saturation magnetic moment of the Fe ions in a field of 10 kG is reduced from 0.8$\mu_B$ for undoped Fe$_3$O$_4$ down to about 0.6$\mu_B$ and 0.1$\mu_B$ for Ag(x)–Fe$_3$O$_4$ with $x$=0.05 and 0.1, respectively. It is also interesting to note that the saturation magnetic moment drops roughly as a quadratic function of $x$. In addition, the coercivity is decreased correspondingly from $\sim$720 G for Fe$_3$O$_4$ to 260 and 85 G for Ag(x)–Fe$_3$O$_4$ with $x$=0.05 and 0.1, respectively. The average magnetic moment of the Fe ions in Fe$_3$O$_4$ is less than the atomic value of 2.0$\mu_B$, which is due to the fact that Fe 3$d$ orbitals hybridize with O 2$p$ orbital and that Fe$^{3+}$ ions align antiferromagnetically at the $A$ and $B$ sites.

Figure 5 plots the integrals of the two negative XMCD features from 703.3 to 709.4 eV (indicated as $B_1$) and from 709.8 to 711.6 eV ($B_2$) and the positive XMCD feature from 709.4 to 709.8 eV ($A$) in the Fe $L_2$-edge XMCD spectra as functions of the amount of Ag in Ag(x)–Fe$_3$O$_4$ and the amount of Al in the Al(x)–Fe$_3$O$_4$ (Ref. 10) to compare the effect of Ag and Al dopants on the magnetic properties of Fe$_3$O$_4$. It shows that the intensities of negative XMCD features decrease significantly and the intensity of the positive XMCD feature remains nearly constant (decreases slightly) as the Ag (Al) concentration increases, revealing that both Ag and Al dopings reduce the overall magnetic moment of Fe ions in the Fe$_3$O$_4$. The integrated intensity of feature $B_1$ at the Fe $L_2$-edge XMCD of Ag(x)–Fe$_3$O$_4$ decreases more rapidly than that of Al(x)–Fe$_3$O$_4$, which can be attributed to a different structural property of the Al dopants.

The ferromagnetic materials are composed of magnetic domains. The lining up of Fe spins within a given domain may be due to delocalized majority-spin ($\uparrow$ spin) Fe 3$d_{eg}$ states by doped magnetanes.\textsuperscript{20} The embedded Ag granules have three plausible effects on the electronic and magnetic properties of Fe$_3$O$_4$. The first effect is that the conduction, i.e., itinerant, states of Ag granules can couple with delocalized $\uparrow$-spin Fe 3$d_{eg}$ states, which reduces the spin polarization of these Fe 3$d_{eg}$ states and consequently weakens the magnetic coupling of Fe spins. This coupling between Ag itinerant and delocalized Fe 3$d_{eg}$ $\uparrow$-spin $\epsilon_g$ states also reduces greatly the resistivity of the films as observed by Hsu \textit{et al.}\textsuperscript{5} The second effect is that the interface-dipole induced electron transfer stated previously reduces the spin moment of Fe ions. The third effect is that the embedded Ag granules may hinder the lining up of the polarization of magnetic domains when a magnetic field is applied, because the lining up of magnetic domains concerns the movement of domain boundaries. These combined effects cause the saturation magnetic moment to drop so rapidly with $x$ as shown in the magnetic hysteresis measurement.

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\textsuperscript{1}E. J. Verwey and P. Haayman, Physica (Amsterdam) 8, 979 (1941).

FIG. 5. Representative integrals of the two negative and one positive features in Fe $L_2$-edge XMCD spectra as functions of $x$ for Ag(x)–Fe$_3$O$_4$ and Al(x)–Fe$_3$O$_4$ (Ref. 10), respectively.