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Investigation of the valence states of Fe and Co in $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ ($0 < x < 1$) thin films by x-ray absorption spectroscopy

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Abstract

The unusual magnetic properties of thin films of $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ ($0 \leq x \leq 1$) ferrite solid solutions have been explained through an investigation of their electronic structure. The x-ray absorption near-edge structure (XANES) spectra of the Fe L_3 -edge and K-edges show that Co replaces Fe^{3+} in the tetrahedral (T_d) sites up to $x = 0.34$ and octahedral (O_h) sites from $0.39 < x < 0.89$. The Co L_3 -edge and O K-edge results indicate mixed valence states of Co as it replaces Fe at dissimilar sites. From the results, it is concluded that the magnetic properties of the thin films of the spinel $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ arise from the Fe^{3+} at the T_d sites. The replacement of Fe^{3+} and Fe^{2+} by Co at the O_h sites results in a crossover to the rocksalt structure and a loss of the magnetic properties.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Thin films of $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ ($0 \leq x \leq 1$) ferrites have been found to exhibit a drop in their magnetic moment by nearly 30% at $x = 0.34$ [1, 2] and to have no magnetic response beyond $x = 0.49$ [2]. On the other hand no such change is observed in the bulk ferrites. X-ray diffraction (XRD) measurements show that the d -spacing remains unchanged at 8.36 Å for the films with $x = 0-0.4$ [2]. An abrupt increase of d -spacing to 8.5 Å is seen at $x = 0.49$ followed by a slow increase to 8.58 Å as x is increased further. This might happen when Co^{2+} and Co^{3+} ions, which have different cationic radii and symmetry, replace Fe at O_h and T_d sites in a specific ratio. XRD patterns (not presented here) do not show additional peaks corresponding to CoO phases, indicating that Co substitutes Fe in the lattice causing the observed structural changes. We therefore undertook an investigation of this unusual magnetic behavior through a study of the electronic structure of these same thin films using XANES spectroscopy and the results are presented here.

2. Experimental details

All thin film samples investigated here, i.e. Fe_3O_4 , CoO standards, and series of $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ ($0 \leq x \leq 1$) were deposited on MgO(001) substrates by a plasma-oxygen assisted molecular beam epitaxy (MBE) as reported by Chern *et al* [3]. The thickness of the films was fixed at ~ 1200 Å. Reflection high-energy electron diffraction (RHEED) and x-ray diffraction (XRD) were used for *in situ* and *ex situ* characterization respectively to ascertain the crystalline quality of the films. XANES measurements were performed at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan operated at 1.5 GeV with a maximum stored current of 200 mA. The transition metal (TM) L-edge and oxygen K-edge were measured at the high-energy spherical grating monochromator (HSGM) BL20A1 beamline (resolving power $E/\Delta E = 8000$) in ultrahigh vacuum ($< 5 \times 10^{-9}$ Torr) in the total electron yield (TEY) mode. The hard x-ray measurements were recorded with a spacing of 0.3 eV for the XANES in the fluorescence yield (FY) mode using a Lytle detector at room temperature, using a Si(111) double crystal monochromator in

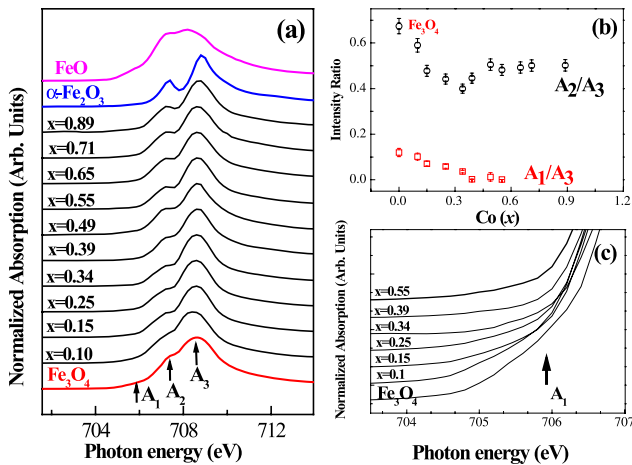


Figure 1. (a) Fe L₃-edge XANES spectra of a series of Fe_{1-x}Co_xO_y thin films, along with FeO, α -Fe₂O₃, and Fe₃O₄ standards. These spectra were normalized to the peak of highest intensity (A₃). (b) The ratios of the intensity of the A₂/A₃ and A₁/A₃ peaks as a function of Co concentration (x). (c) An expanded view of the peak A₁ region to show that the peak diminishes beyond $x = 0.39$.

the Wiggler-C (17C) beamline. All spectra were normalized to a unity step height in the absorption coefficient from well below to well above the edge. Standard oxide films of Fe₃O₄, Fe₂O₃, Co₂O₃, Co₃O₄, and CoO were used for energy calibration and also for comparing the different electronic valence states.

3. Results and discussion

The Fe L₃-edge ($j_{\text{core}} = 3/2$) XANES spectra presented in figure 1(a) are transitions from the 2p_{3/2} levels to the 3d unoccupied state with spin-orbit coupling. The spectra exhibit a multi-peak structure with a large peak at 708.5 and a shoulder at 707 eV, which may be attributed to crystal-field splitting [4–10]. As in earlier reports, the L₃-edge of Fe₃O₄ contains three prominent features marked A₁, A₂, and A₃ corresponding to Fe²⁺ in the O_h site, Fe³⁺ in the T_d site, and Fe³⁺ in the O_h site, respectively [5–9]. The curves are normalized at the A₃ intensity. The weak A₁ feature appears reduced in intensity as x is increased. The A₁/A₃ peak ratio given in figure 1(c) is found to decrease slightly up to $x = 0.34$ and is nearly constant for $x = 0.34$ –0.49. This may be a result of the reduction of both the A₁ and A₃ peaks as Fe²⁺ and Fe³⁺ from the O_h sites are replaced by Co. The A₁ peak is not discernable beyond $x = 0.49$. At the same time the A₂/A₃ ratio also reduces rapidly (figure 1(b)) meaning a reduction of the A₂ peak with an increase of x , showing a minimum at $x = 0.34$ and indicating replacement of Fe³⁺ by Co at T_d sites [5]. The spectra remain unchanged at $x = 0.39$ –0.49, indicating a possible filling of both the Fe²⁺ and Fe³⁺O_h sites simultaneously (and also as a result of the normalization at the A₃ intensity). A steep increase of the A₂/A₃ ratio is seen at $x = 0.49$ followed by a slow increase with further increase of x , indicating the replacement of Fe at the O_h sites. This leads to a decrease of A₃ intensity with no change in that of A₂, resulting in an increase of the A₂/A₃ ratio, as seen

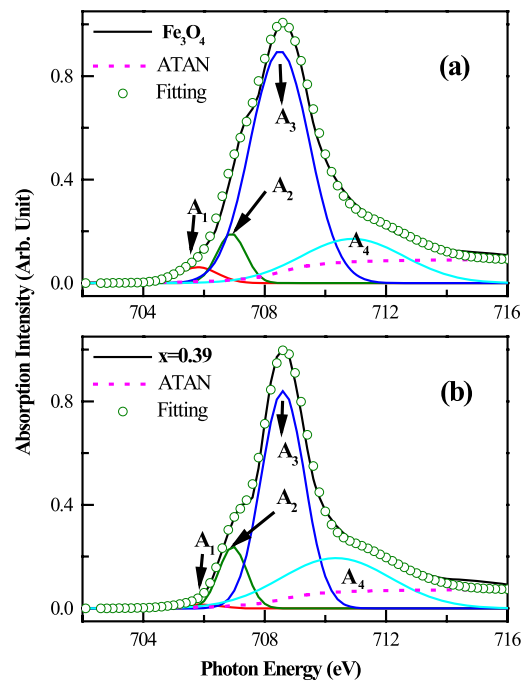


Figure 2. The curve fitting of the L₃-edge spectra for (a) Fe₃O₄, $x = 0$ and (b) $x = 0.39$ in with 4 G (A₁₋₄) and an arctangent function to separate the close lying peaks A₁, A₂, and A₃.

in figure 1(b). This is further confirmed from a very small increase of the A₁/A₃ ratio at $x = 0.39$ –0.49 where the sharp increase of A₂/A₃ is seen. The spectra are of nearly identical line shapes from $x = 0.49$ to 0.89 and closely resemble that of α -Fe₂O₃. These results are consistent with the XRD data [2] in which no major change was seen in the spinel structure up to $x = 0.49$. The similarity between figure 4(b) and the M_s and H_c curves in [2] for $x = 0$ –0.34 indicates the possible role of Fe³⁺ in the T_d sites in the unusual magnetic properties of these ferrite films. A steep rise at $x = 0.49$ is followed by a slow increase for $x > 0.49$. These spectra thus clearly indicate a transition of the Fe sublattice from Fe₃O₄ to α -Fe₂O₃.

The spectra of figure 1(a) were fitted to separate the close lying peaks A₁, A₂, and A₃ as shown in figures 2(a) and (b) for Fe₃O₄, $x = 0$ and 0.39 given as examples. Each edge has been represented by two functions, arctangent (edge jump for step function) and Gaussian (absorption white line), as is generally done in XANES spectral curve fitting (in order to account for the absorption edge and the transition to the 3d states). The A₁ feature is clearly seen in figure 2(a) but nearly becomes extinct at $x = 0.39$ as shown in figure 2(b), which is not easily discernable in figure 1(a). The A₄ feature is not discussed here due to the complex character of this region. The areas under the curves were used to obtain the ratios A₁/A₃ and A₂/A₃ presented in figures 1(b) and (c) respectively. A similar procedure was adopted in the case of the spectra presented in figure 5.

Figure 3 shows the normalized Fe K-edge spectra. The main peaks between 7130 and 7135 eV are associated with the transition of the Fe 1s electron to empty 4p states. The pre-edge feature near 7115 eV is associated with the transition of the Fe 1s electron to empty 3d states (quadrupole-allowed transition).

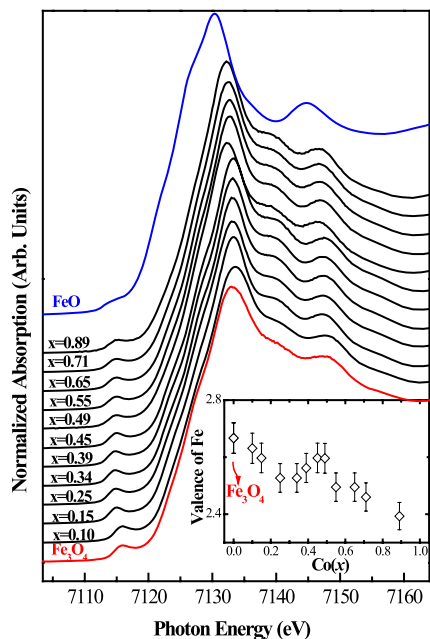


Figure 3. Normalized Fe K-edge XANES spectra at different x values along with Fe_3O_4 films and FeO bulk. The inset is the variation of the valence of the Fe ion with x as obtained from the chemical shift of spectra.

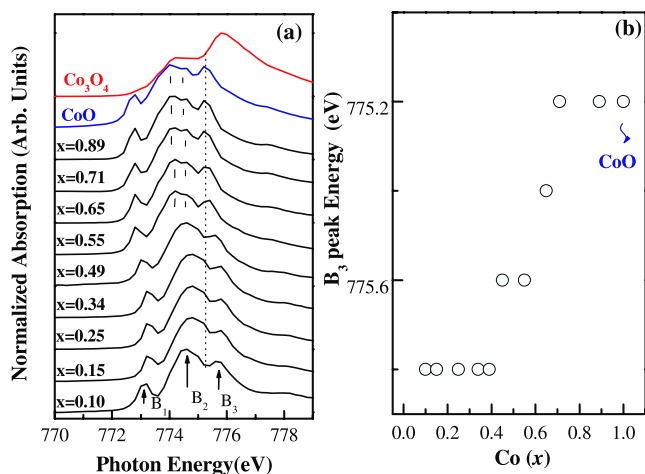


Figure 4. (a) Co L_3 -edge XANES spectra of a series of $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ thin films and CoO and Co_3O_4 standards. These spectra were normalized to the peak of highest intensity (B_3). (b) The photon energy shifts of the B_3 peak as a function of Co concentration (x).

The spectral shapes of all the curves are basically unaffected by the changes in x . This demonstrates that the spectral line shape of the samples is similar to Fe_3O_4 . On the other hand, the maximum peak position is shifted to the lower energy side as x increases, indicating a decrease in the valence of Fe. The variation of the average valence of Fe is plotted as a function of x in the inset of figure 3. It is seen that the valence decreases from 2.667 of Fe_3O_4 , and reaches a minimum of +2.5 at $x = 0.34$. It indicates that the 1/3 part of Fe is replaced at the Fe^{3+} T_d sites by Co at $x = 0.34$. The valence again increases with further doping to a maximum of +2.66 at $x \sim 0.5$, and

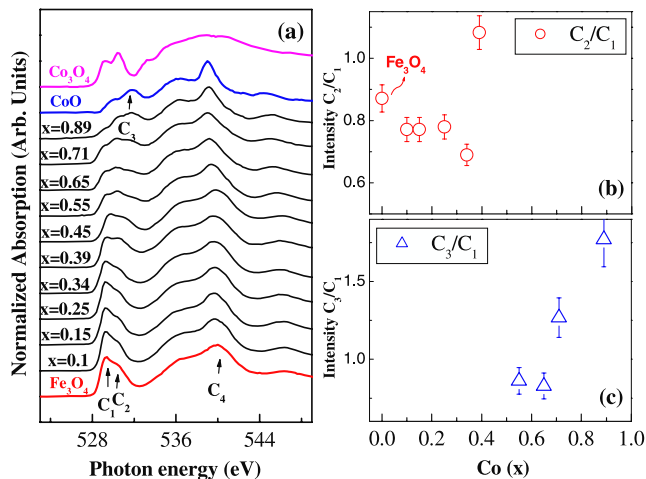


Figure 5. (a) O K-edge XANES spectra of a series of $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ thin films and the standards CoO , Co_3O_4 , and Fe_3O_4 . These spectra were normalized to the main peak C_4 . (b) The ratio of peaks C_2/C_1 , and (c) the ratio of peaks C_3/C_1 .

decreases on further increase of x to 2.4. This decrease may be a result of the crossover of the structure to rocksalt as Fe is replaced by Co up to $x = 0.89$. The bump in the valence curve at $x = 0.3$ – 0.49 is a likely result of Fe replacement at the O_h sites discussed above. Thus the Fe K-edge results are consistent with the Fe L_3 -edge results as discussed above in terms of the replacement of Fe at T_d and O_h sites.

Figure 4(a) shows the Co L_3 -edge XANES spectra which exhibit three features marked B_1 , B_2 , and B_3 which are consistent with the calculated crystal-field $10 D_q$ results [10, 11] for different valence states in the T_d and O_h symmetry. The spectra of the films for $x < 0.49$ resemble the CoO spectrum (indicative of Co^{2+}) with an additional peak B_3 (around 775.8 eV) which corresponds to Co_3O_4 , indicating a Co^{3+} contribution also. Therefore, it is reasonable to believe that not only divalent but also trivalent Co ions replace Fe in the Fe_3O_4 up to $x = 0.34$ as indicated above. With $0.34 < x < 0.49$, B_3 gradually shifts to lower energy (towards CoO). With further increase in x , the spectral shapes are similar to CoO (rocksalt structure and O_h symmetry). These results are consistent with those of the Fe L_3 -edge discussed above. In addition, the variation of the B_3 position changes with x (figure 4(b)) are similar to the d -spacing results [2], indicating the influence of Co valence changes on the crystal structure. The presence of a peak B_3 attributable to the Co^{3+} valence state (Co_3O_4) in these films is noteworthy as the same is not found in bulk, as mentioned earlier. The absence of peaks corresponding to purely CoO or Co_3O_4 in these spectra confirms the XRD result on phase purity of the films [2]. These results indicate that both Co^{2+} and Co^{3+} replace Fe^{3+} initially ($x \leq 0.34$). The initial flat portion of the B_3 peak variation with x is similar to the XRD results [2], indicating that this does not result in a change to the spinel structure. The later part of the curve shows an increase similar to that of the XRD which may be a result of the crossover of the crystal structure to rocksalt in the presence of octahedral CoO .

Figure 5 shows the XANES O K-edge spectra of $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ for various values of x , along with Fe_3O_4 , Co_3O_4 , and CoO standard films. All the spectra are normalized to the highest peak at C_4 at ~ 540 eV. These spectra provide the partial density of the O 2p states at the oxygen sites, which are hybridized with TM 3d and sp bands and are sensitive to the local structure and the type of nearest neighbors. The relatively narrow pre-peak feature in the photon energy range 528–533 eV is due to the transition of electrons from O 1s to the unoccupied O 2p states that are hybridized with the TM 3d states [12]. The spectra consist of three major components labeled C_1 , C_2 , and C_3 which exhibit changes as Co content is increased [13–15]. The C_3 peak can be assigned to the t_{2g} band from the splitting of d orbitals at CoO hybridized bands [16]. As x increases, the C_3 peak intensity increases, the pre-peak becomes broader. The ratio of C_1/C_2 peaks decreases with an increase of x , also showing a minimum at $x = 0.34$ (figure 5(b)). This is similar to the Fe result (figure 1(b)) and may mean that Co is replacing Fe in T_d sites. On further increase of x , the features slowly change to that of the CoO spectrum. The ratio of the C_3/C_1 peaks increases as x is increased from 0.49 to 0.89 (figure 5(c)) similar to the case of the Co L_3 -edge (figure 4(b)). Thus the O K-edge spectra are found to confirm the changes in the Fe L_3 -edge at low Co content and the Co L_3 -edge at high Co content and therefore support the conclusions drawn above. The results presented here show that an increased incorporation of Co^{3+} into the O_h sites from $x = 0.34$ to 0.49 and beyond transform the spinel into a rocksalt structure which may be attributed to the observed reduction of the ferromagnetic nature of these films.

4. Conclusion

From a detailed investigation of ferrite thin films by XANES, it is concluded that incorporation of Co^{3+} and Co^{2+} in the films of $\text{Fe}_{1-x}\text{Co}_x\text{O}_y$ with $x > 0.45$ plays an important role in making their magnetic response quite different from the bulk CoFe_2O_4 . The results thus confirm that the observed unusual magnetic properties of the ferrite thin films, namely the decrease of magnetic response up to $x = 0.34$, is due to the replacement of Fe^{3+} by Co at T_d sites and the near absence

beyond $x = 0.49$ is a result of further replacement of Fe at O_h sites by Co, resulting in a crossover of the structure from spinel to a rocksalt.

Acknowledgments

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