Antiferromagnetic-to-ferromagnetic transition induced by diluted Co in SrFe$_{1-x}$Co$_x$O$_3$:
Magnetic circular x-ray dichroism study

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The antiferromagnetic-to-ferromagnetic transition in SrFe$_{1-x}$Co$_x$O$_3$ ($x = 0.15$) induced by Co doping has been studied by magnetic circular x-ray dichroism. The orbital and spin magnetic moments of the Fe and Co 3$d$ states under the magnetic field of 2 T are found to show different $x$ dependences: The spin polarization of Fe 3$d$ gradually increases with Co concentration; on the other hand, a large spin polarization of Co 3$d$ is induced already in the antiferromagnetic phase, indicating that the Co moment is nearly fully aligned already in the antiferromagnetic phase. This suggests that the alignment of the Fe magnetic moment in SrFe$_{1-x}$Co$_x$O$_3$ is induced by interaction with doped Co magnetic moment. Possible formation of ferromagnetic Co rich region is discussed.

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I. INTRODUCTION

Ferromagnetic transition-metal oxides with high Curie temperatures ($T_C > 300$ K) have been the subject of extensive research because of their scientific interest as well as technological importance. The origin of the ferromagnetism and the magnetotransport properties, however, has been controversial in many cases. For example, in the perovskite-type Mn oxides, since both electron-electron interaction and electron-phonon interaction are strong, the origin of the “colossal” magnetoresistance has been discussed in terms of double exchange,$^1$ magnetic polarons,$^2$ phase competition,$^3$ etc. The magnetic properties of systems where transition metals are diluted have been found even more intriguing. For examples, in SrRu$_{0.5}$Mn$_{0.5}$O$_3$, it has been reported that the effective magnetic moment of the Ru ion is enhanced by ferromagnetic interaction with the Mn ions.$^4$ Recently, ferromagnetism with high Curie temperature has been observed in systems where a low concentration of Co or V are substituted in ZnO, i.e., in the diluted magnetic semiconductor Zn$_{1-x}$Co$_x$O and Zn$_{1-x}$V$_x$O.$^5,6$

In the solid-solution system SrFe$_{1-x}$Co$_x$O$_3$, an interesting antiferromagnetic-to-ferromagnetic transition as a function of Co concentration $x$, and a high Curie temperature of $T_C = 300$ K have been reported.$^7$ SrFeO$_3$ is an antiferromagnet ($T_N = 134$ K) and the spin structure is of a screw type with a wave vector along the (111) axis. With Co doping, SrFe$_{1-x}$Co$_x$O$_3$ exhibits ferromagnetism for $x > 0.1-0.15$. The magnetization of SrFe$_{1-x}$Co$_x$O$_3$ gradually increases with $x$ and becomes the largest at $x = 0.2$. The transition temperature becomes the highest $\sim 340$ K at $x = 0.6$. The composition dependence of saturation magnetization for $x > 0.4$ is consistent with a simple ionic picture if it is assumed that Fe$^{4+}$ ions with $4\mu_B$ and Co$^{4+}$ ions with $1.8\mu_B$ are coupled ferromagnetically$^7$ [see Fig. 1(a)]. The hyperfine field at the Fe nuclei in the magnetically saturated state, which is 330 kOe for SrFeO$_3$, decreases at first ($x \leq 0.15$) quickly and then slowly to about 290–300 kOe as the Co content increases. Based on this observation, it was suggested that the Co substitution tends to delocalize electrons of the Fe parentage in a broadened $\sigma^*$ band.$^7$ According to an x-ray diffraction study, SrFe$_{1-x}$Co$_x$O$_3$ maintains the cubic perovskite structure in the whole Co concentration range $x$, while the concentration dependence of the lattice parameter shows a sudden decrease at $x = 0.3-0.4$.$^7$

Magnetic circular x-ray dichroism (MCXD) in core-level soft x-ray absorption is a powerful method to obtain information about the magnetic states at each atomic site. With use of MCXD sum rules, the orbital and spin magnetic moments on each atom can be deduced. A previous MCXD study of SrFe$_{0.5}$Co$_{0.5}$O$_3$ has demonstrated the small and large orbital magnetic moments at Fe and Co sites, respectively.$^5$ In this paper, a series of SrFe$_{1-x}$Co$_x$O$_3$ samples ($0 \leq x \leq 0.5$) have been studied by MCXD at low temperature (30 K) under a magnetic field (2 T). Based on the orbital and spin magnetic moments of the Fe 3$d$ and Co 3$d$ states thus deduced, we shall discuss the electronic structure of the Fe 3$d$ and Co 3$d$ states in SrFe$_{1-x}$Co$_x$O$_3$ and the mechanism of the antiferromagnetic-to-ferromagnetic transition.

II. EXPERIMENT

Sintered polycrystalline samples of SrFe$_{1-x}$Co$_x$O$_3$ ($0 \leq x \leq 0.5$) were prepared from SrCO$_3$, $\alpha$-Fe$_2$O$_3$, and Co$_3$O$_4$ powders, each with purity of 99.9% [except for SrCO$_3$ (Ref. 9)] as described elsewhere.$^7$ X-ray diffraction analysis showed that all samples were single-phase.$^7$ The magnetiza-
Magnetic circular x-ray dichroism in the Fe $^{2+}$ core-level absorption spectroscopy measurements were made in the total-electron-yield mode using circularly polarized synchrotron radiation from the undulator beam line BL23SU of SPring-8. Energy resolution was $\sim 130$ meV at $h\nu = 800$ eV. The sample chamber was kept at 2 $\times$ 10$^{-8}$ Pa. Before each series of MCXD measurements, a fresh surface was exposed by scraping with a diamond file in the ultrahigh vacuum. The measurements were carried out at 30±0.1 K, which was well below $T_C$ for the $x \geq 0.2$ samples. Using a superconducting magnet, a magnetic field of ±2 T, which was enough to saturate the magnetization of the $x \geq 0.2$ samples [see Fig. 1(b)], was applied to the sample parallel and antiparallel to the propagation vector of the incident light. For each $x$, we performed several sets of MCXD measurements to check the reproducibility. The degree of circular polarization was estimated to be $\geq 95\%$ by comparing measured Ni $2p$ MCXD of Ni metal with the reported MCXD intensities. The incident photon flux was monitored using an Au mesh placed behind the prefocusing mirror.

III. RESULTS AND DISCUSSION

Figure 2 (upper panel) shows the Fe $2p$ x-ray absorption spectroscopy (XAS) spectra for photon helicity parallel ($\mu^+$) and antiparallel ($\mu^-$) to the Fe 3d majority-spin direction. MCXD spectra $(\Delta \mu = \mu^+ - \mu^-)$ and their energy integrals are shown in the lower panel of Fig. 2. Figure 3 also shows the Co $2p$ XAS spectra $\mu^+$ and $\mu^-$, MCXD spectra $\Delta \mu$, and their energy integrals. The Fe $2p$ XAS spectra indicate that the Fe$^{4+}$ ions (3$d^6$) are in the high-spin states hybridized with the high-spin 3$d^6$ configuration (where $L$ denotes a ligand hole) and the Co $2p$ XAS spectra indicate that the Co$^{4+}$ ions are primarily in the intermediate-spin states hybridized with the 3$d^6$ configuration, as Abbate et al. reported.

The energy integral of the MCXD spectra is proportional to the orbital magnetic moment at the atomic site. As shown in Figs. 2 and 3, the Fe (Co) $2p$ MCXD spectra do not show changes in the line shapes and the relative intensities of the Fe (Co) $2p_{3/2}$ and $2p_{1/2}$ peaks in the whole Co concentration range. Therefore, we consider that the MCXD intensity at the Fe (Co) $2p_{3/2}$ peak is proportional to the magnetization at the Fe (Co) site. Figure 2 shows that the MCXD intensity at the Fe $2p_{3/2}$ peak ($\sim 711$ eV) becomes stronger as the Co concentration $x$ increases, while the energy integral remains a very small positive value in the whole concentration range. This indicates that the orbital magnetic moment of the Fe 3$d$ states is nearly zero in the whole Co concentration range. This is normally expected for the highly charge transferred 3$d^6$ configuration, consistent with the previous reports.

Figure 3 shows the Co $2p$ MCXD spectra of SrFe$_{1-x}$Co$_x$O$_3$. In contrast to the Fe $2p$ MCXD, the MCXD intensity at the Co $2p_{3/2}$ peak ($\sim 781$ eV) is substantial already for $x=0.1$ and does not show strong $x$ dependence.
Given in the units of m. D M orb where the nominal Co 4+ ion is in the highly charge transferred 3-electron shell. This is consistent with the proposition that the Co 3 whole concentration range. This means that the orbital magnetic moments of Fe 3d and of Co 3d are proportional to the degeneracy of the core level. In estimating the spin magnetic moment from Eq. (2) we have to separate the Fe 3d and Co 3d XAS shows a minimum. Furthermore we take into account the correction factor for the spin sum rule [Eq. (2)] according to Teramura et al. [110.685 for Fe 3+ (d5) and 1/0.874 for Co 3+ (d6), the number of effective d electrons is considered]. M T in Eq. (2) is estimated to be very small (<1% of M spin) according to a ligand-field theoretical calculation. Also, since our measurements were made on polycrystals, the angle average would result in a vanishing magnetic-dipole term. Therefore, we have ignored M T in estimating the spin magnetic moment from Eq. (2). N 3d was deduced to be 4.85 for Fe and 5.8 for Co obtained from the cluster-model analyses.

Figure 4 shows the orbital M orb, spin M spin, and total M total magnetic moments of the Fe 3d orbitals (a) and of the Co 3d orbitals (b) as functions of Co concentration x obtained using the MCXD orbital (Ref. 12) and spin sum rules (Ref. 13). Correction factors (Ref. 14) are applied in estimating M spin.

With increasing Co concentration, it somewhat increases for x = 0.2 but slowly decreases for x ≥ 0.2. The energy integral of the Co 2p MCXD spectra is strongly negative in the whole concentration range. This means that the orbital magnetic moment and the spin magnetic moment are parallel in the Co 3d states, as expected for a more-than-half-filled d-electron shell. This is consistent with the proposition that the nominal Co 4+ ion is in the highly charge transferred 3d6L configuration.

By applying the orbital and spin sum rules to the MCXD spectra, the orbital (M orb) and spin (M spin) magnetic moments of the Fe and Co 3d states have been estimated using

\[ M_{\text{orb}} = -2 \frac{\Delta A_{L_3} + \Delta A_{L_2}}{3(A_{L_3} + A_{L_2})} (10 - N_{3d}), \]

\[ M_{\text{spin}} + 7 M_T = -\frac{\Delta A_{L_3} - 2\Delta A_{L_2}}{A_{L_3} + A_{L_2}} (10 - N_{3d}), \]

where M orb, M spin, and the magnetic-dipole moment M T are given in the units of \( \mu_B/\text{atom} \), N 3d is the 3d electron occupation number, \( \Delta A_{L_3} \) and \( \Delta A_{L_2} \) are the energy integrals of the 2p 3/2 and 2p 1/2 MCXD intensities, and A L3 and A L2 are the energy integrals of the 2p 3/2 and 2p 1/2 XAS intensities. In estimating the XAS intensities, background has been subtracted from the average XAS spectra \( \left[ \left( \mu^+ + \mu^- \right)/2 \right] \). The background is due to transition to the continuum states above the Fermi level and is composed of two steps functions at the Fe (Co) 2p 3/2 and 2p 1/2 XAS peaks with the intensity proportional to the degeneracy of the core level. In estimating the spin magnetic moment from the XAS and MCXD spectra, we have to separate the Fe (Co) 2p MCXD spectra into the 2p 3/2 and 2p 1/2 components. We have divided the Fe (Co) 2p spectra into the two components at 720 (791) eV, where the Fe (Co) 2p XAS shows a minimum. Furthermore we take into account the correction factor for the spin sum rule [Eq. (2)] according to Teramura et al. [110.685 for Fe 3+ (d5) and 1/0.874 for Co 3+ (d6), the number of effective d electrons is considered]. M T in Eq. (2) is estimated to be very small (<1% of M spin) according to a ligand-field theoretical calculation. Also, since our measurements were made on polycrystals, the angle average would result in a vanishing magnetic-dipole term. Therefore, we have ignored M T in estimating the spin magnetic moment from Eq. (2). N 3d was deduced to be 4.85 for Fe and 5.8 for Co obtained from the cluster-model analyses.

Figure 4 shows the orbital M orb, spin M spin, and total M total magnetic moments of the Fe 3d orbitals (a) and of the Co 3d orbitals (b) as functions of Co concentration x obtained using the MCXD orbital and spin sum rules. For the Fe site, M spin and M total increase monotonously in the antiferromagnetic phase (x ≤ 0.15) and then continue to increase in the ferromagnetic phase (x ≥ 0.15). M orb is slightly negative but almost quenched in the whole Co concentration range. Since SrFeO 3 is a helical antiferromagnet (\( T_N \sim 134 \) K), the increase of the spin and total magnetic moment of Fe 3d for x < 0.15 is probably due to canting of the magnetic moment toward the applied field.
For the Co site, \( M_{\text{spin}} \) and \( M_{\text{total}} \) become as large as those in the ferromagnetic phase already in the antiferromagnetic phase \( (x=0.1) \), suggesting that the Co moments are fully aligned under the magnetic field of 2 T even in the antiferromagnetic state. Therefore, it appears that the Fe and Co subsystems behave rather independently and are only weakly coupled (at least in the antiferromagnetic phase) but that the weak coupling is sufficient for the Co subsystem to induce ferromagnetism in the Fe subsystem for \( x > 0.2 \). The mechanism of how the magnetization of Co becomes large even for small \( x \) is not clear at present. There must be strong ferromagnetic interaction between Co atoms already for \( x = 0.1 \). One possibility is that the doped Co atoms are not uniformly distributed but some of them are located close to each other, that is, they form Co-rich regions on a microscopic scale and interact strongly with each other, leading to the ferromagnetic alignment, but it is not possible for x-ray diffraction to detect the inhomogeneous distribution of Co atoms.

One can also notice in Fig. 4(b) that \( M_{\text{spin}} \) and \( M_{\text{total}} \) of Co show nonmonotonous behavior in the ferromagnetic phase. They decrease as the Co concentration increases in the ferromagnetic phase but show a sudden increase at \( x = 0.4 \), corresponding to the anomaly observed in the magnetization measurement [Fig. 1(a)]. As for \( M_{\text{orb}} \) of the Co 3d states, it remains constant or slightly increases with \( x \) for \( x \leq 0.2 \) but decreases monotonously in the ferromagnetic phase as shown in Fig. 4(b). The orbital and spin magnetic moments of the Co\(^{4+}\) ion have been predicted by the ionic model for the three different spin states: \( M_{\text{orb}} = 0.86 \mu_B/\text{Co}, M_{\text{spin}} = 0.38 \mu_B/\text{Co} \) for the low-spin state (LS); \( M_{\text{orb}} = 0.01 \mu_B/\text{Co}, M_{\text{spin}} = 4.96 \mu_B/\text{Co} \) for the high-spin state (HS); \( M_{\text{orb}} < 1 \mu_B/\text{Co}, M_{\text{spin}} \sim 3 \mu_B/\text{Co} \) for the intermediate-spin state (IS). From this information and the experimental values of \( M_{\text{orb}} \) and \( M_{\text{spin}} \), the Co atoms are thought to be primarily in the IS state in the whole Co concentration range, but the weight of the LS state increases with \( x \). Alternatively, the decrease of the Co 3d orbital magnetic moment in the ferromagnetic phase can also be explained by the increase of the itinerancy with \( x \).

The total magnetic moment of SrFe\(_{1-x}\)Co\(_x\)O\(_3\) estimated using MCXD sum rules are compared with the SQUID measurement in Fig. 5. Although the overall behavior including the \( x \approx 0.3 \) anomaly is qualitatively reproduced, the absolute value estimated by MCXD is nearly half of the magnetization of the O 2p electrons is also substantial since there is strong 3d-2p hybridization. Indeed finite MCXD signals have been observed for the O 1s absorption edge in the case of La\(_{1-x}\)Sr\(_x\)MnO\(_3\). The orbital magnetic moment of the O 2p electrons is not sufficient to fill the shortage of the magnetization of 0.5\( \mu_B \) since it is at most 0.1\( \mu_B \) even in the manganites. Since the magnetic moment of the O 2p orbitals is induced by the mixing with the transition-metal d orbitals, the spin magnetic moment of the O 2p electrons which is expected to be larger than the orbital magnetic moment should be considered. At present, however, there is no way to estimate the spin magnetic moment of the O 2p electrons by using the MCXD sum rules. Another possible cause is that the magnetization is reduced at the surface compared to that in the bulk due to scraping. Since the effective probing depth of the XAS measurement is at most 10 nm in the total-electron-yield method, the estimated magnetization in transition-metal oxides may be substantially influenced by the electronic states of the scraped surfaces. Therefore, the estimated magnetization may increase by using cleaved samples or single-crystalline film samples.

IV. CONCLUSION

SrFe\(_{1-x}\)Co\(_x\)O\(_3\) \((0 \leq x \leq 0.5)\) has been studied by MCXD in the Fe 2p and Co 2p core-level absorption spectra across the antiferromagnetic-to-ferromagnetic transition. The magnetic moments of the Fe and Co 3d states are found to show different composition dependences. For the Fe 3d states, the increase of the spin magnetic moment in the antiferromagnetic phase is induced by the applied magnetic field and the internal magnetic field through the canted Fe 3d spins. For the Co 3d states, already in the antiferromagnetic phase \( (x = 0.1) \), the Co moment is fully aligned under the 2 T magnetic field. The Fe and Co subsystems are only weakly coupled at least in the antiferromagnetic phase but the weak coupling is sufficient to induce ferromagnetism in the Fe subsystem in the ferromagnetic phase. In order to understand this behavior, one possible scenario is that the doped Co atoms are not distributed uniformly and Co atoms in Co rich region interact with each other strongly.

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SrCO$_3$ may contain a small amount of Ba (≤0.5%) substituting the Sr site. In the Co 2p XAS spectra of SrFe$_{0.5}$Co$_{0.5}$O$_3$ in Fig. 3, the weak structures at ~785 and 809 eV may be due to the Ba 3$d$ to 4$f$ transition. Since the cross section of this transition is very large, a very small amount of Ba (≤0.5%) can induce observable signals.

For example, MCXD signal in the Ru 3$p$ XAS of a single-crystalline film of the ferromagnetic metal SrRuO$_3$ shows higher intensity (~10% of Ru 3$p_{3/2}$ XAS peak) than that of a sintered polycrystalline sample scraped with a diamond file (~6%) [K. Terai and Y. Takeda (private communication)].