Soft X-ray Magnetic Circular Dichroism in La$_{1-x}$Sr$_x$MnO$_3$ and SrFe$_{1-x}$Co$_x$O$_3$


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We have studied the magnetic and electronic states of La$_{1-x}$Sr$_x$MnO$_3$ and SrFe$_{1-x}$Co$_x$O$_3$ by soft x-ray magnetic circular dichroism (SXMCD) measurements at the Mn, Fe and Co L$_{2,3}$ edges, and the O K core-absorption edges. An application of the SXMCD orbital sum rule to the L$_{2,3}$ SXMCD data clearly shows that the average orbital magnetic moment (m$_{\text{orb}}$) of the nominal Mn$^{3+}$ and Mn$^{4+}$ ions is finite but small in La$_{1-x}$Sr$_x$MnO$_3$, and that m$_{\text{orb}}$ of the nominal Fe$^{3+}$ ion is almost zero whereas m$_{\text{orb}}$ of the nominal Co$^{4+}$ ion is large in SrFe$_{1-x}$Co$_x$O$_3$. An SXMCD was also observed at the O K edge, showing spin polarization of the O 2p state. These results provide evidence that the nominal Mn$^{3+}$, Mn$^{4+}$, Fe$^{3+}$, and Co$^{4+}$ ions are dominantly in the highly charge-transfered d$^5$L$_o$, d$^6$L$_o$, d$^6$L$_u$ and d$^8$L$_u$ configurations, respectively, with L$_o$ denoting the oxygen 2p hole.

Key words: soft x-ray magnetic circular dichroism, perovskite transition-metal oxides, colossal magnetoresistance, charge transfer, d-p hybridization, sum rule, orbital magnetic moment, core-level absorption, electron configuration

1. Introduction

The recent discovery of large or "colossal" magnetoresistance in manganese oxides$^{1,2}$ has aroused renewed interest in the electronic properties of perovskite-type transition-metal (TM) oxides, in particular with regard to the correlation between their electrical and magnetic properties. It has recently been emphasized that the interplay between spin, orbital, and charge could play an important role in understanding the electronic and magnetic states of perovskite-type TM oxides. Undoped insulating parent materials of TM oxides, which are usually antiferromagnetic, are categorized into the Mott-Hubbard or charge-transfer type on the basis of the so-called Zaanen-Sawatzky-Allen diagram$^3$. A large number of experimental and theoretical studies have been made using a variety of methods, in particular spectroscopic techniques such as x-ray and ultraviolet photoemission$^{9,7}$, resonant photoemission$^{9}$, soft x-ray absorption$^{3,7,10}$, electron energy-loss$^{11,12}$, and optical$^{13,15}$ measurements. Some of them indicate or claim the important role of the O 2p state which hybridizes with the TM 3d state. However, direct experimental evidence has yet been scarce for the hybridization-induced large charge transfer in TM oxides, which have undoped parent materials belonging to the charge-transfer type.

Soft X-ray magnetic circular dichroism (SXMCD) in core-level absorption$^{16,18}$ has in the past decade proven to be a powerful technique to probe the orbital and charge states as well as the spin state in multi-component magnetic substances, such as TM oxides. SXMCD measurements allow an element-specific and separate determination of the orbital (m$_{\text{orb}}$) and spin (m$_{\text{spin}}$) magnetic moments in combination with the SXMCD orbital and spin sum rules$^{19,20}$. Since the character of not only the orbital but also the charge states is strongly reflected in values of m$_{\text{orb}}$, an investigation using the SXMCD technique could provide direct information about the orbital and charge states in TM oxides. Several SXMCD measurements have recently been made on ferromagnetic TM oxides$^{21,24}$. However, only a few SXMCD investigations$^{22,23}$ have yet been reported that clarify the above-mentioned aspect.

In this paper we report on an SXMCD study of the electronic and magnetic states of perovskite-type oxides La$_{1-x}$Sr$_x$MnO$_3$ and SrFe$_{1-x}$Co$_x$O$_3$. The results of SXMCD measurements made around the TM L$_{2,3}$ core edges show that the average m$_{\text{orb}}$ of the nominal Mn$^{3+}$ and Mn$^{4+}$ ions is finite but small, m$_{\text{orb}}$ of the nominal Fe$^{3+}$ ion is almost zero and m$_{\text{orb}}$ of the nominal Co$^{4+}$ ion is large. We have also observed a clear SXMCD at the O K core edge, which shows strong spin polarization of the O 2p hole. These findings provide experimental evidence for the TM 3d-O 2p hybridization-induced, highly charge-transfered ground state with the Mn d$^5$L$_o$, Fe d$^6$L$_u$, and Co d$^8$L$_u$ configurations in both compounds.
2. Experiments

Polycrystalline samples of La$_{1-x}$Sr$_x$MnO$_3$ (x=0.2 and 0.5) and SrFe$_{1-x}$Co$_x$O$_3$ (x=0.2 and 0.4) were prepared by solid-state reaction, the details of which were described elsewhere$^{5,25}$. The SXMCD experiments were made around the Mn, Fe, and Co L$_{2,3}$ (2p$_{1/2,3/2}$→3d) core-absorption edges at ~90K well below the Curie temperature using circularly polarized synchrotron radiation on soft x-ray helical undulator beamline ARINE1B at the Photon Factory, High Energy Accelerator Research Organization. Polarization-dependent x-ray absorption spectra (XAS) were measured at a base pressure of ~7x10$^{-10}$Torr using the total electron-yield method. The sample surface was cleaned by diamond filing just before each measurement. The photon helicity of the incident light was fixed and the magnetic-field direction was reversed parallel and antiparallel to it. A magnetic field of ±1.1T was applied to the sample perpendicularly to the surface using a permanent-magnet SXMCD apparatus for each photon energy. The SXMCD measurements were also made at the O K (1s→2p) core edge at a lower temperature of 20K and under a higher magnetic field of ±2T using an ultrahigh-vacuum superconducting magnet. The width of both the entrance and exit slits of the monochromator was set at ~40 μm, giving an energy resolution of ~1eV at the Fe and Co L$_{2,3}$ edges. The degree of circular polarization ($P_c$) of the light incident onto the sample was calculated to be ~95% around the first-harmonic energy of the undulator radiation (hv) and at lower energies within ~100 eV of hv. The photon flux emerging from the monochromator was monitored using the photocurrent from an Au mesh placed just downstream of a post-focusing mirror on the beamline.

3. Results and Discussion

The flux-normalized polarization-dependent XAS spectra (μ$_+$ and μ-) around the Mn L$_{2,3}$ core edges in La$_{0.8}$Sr$_{0.2}$MnO$_3$ are shown in Fig. 1(a). Figures 2 (a) and 3 (a) display the polarization-dependent Fe and Co L$_{2,3}$ XAS spectra, respectively, in SrFe$_{0.6}$Co$_{0.4}$O$_3$. Here, μ$_+$ (solid curve) and μ$_-$ (dashed curve) stand for the absorption coefficients for the photon helicity parallel and antiparallel to the spin direction of the 3d majority electrons, respectively. A correction for $P_c$ was made using a calculated value of $P_c$ = 95%. The SXMCD spectrum (Δμ=μ$_+$-μ$_-$) around the Mn L$_{2,3}$ core edges in La$_{0.8}$Sr$_{0.2}$MnO$_3$ is shown by the bold solid curve in Fig. 1(b). The bold solid curves in Figs. 2(b) and 3(b) display the Fe and Co L$_{2,3}$ XAS spectra in SrFe$_{0.6}$Co$_{0.4}$O$_3$, respectively. These SXMCD spectra have been deduced from the XAS spectra in Figs. 1(a), 2(a), and 3(a). The integrals of the SXMCD spectra over energy (∫Δμdω) are shown by thin solid curves in Figs. 1(b)-3(b).

Fig. 1 (a) Polarization-dependent Mn L$_{2,3}$ XAS spectra of La$_{0.8}$Sr$_{0.2}$MnO$_3$. The solid and dashed curves denote the XAS spectra for the photon helicity parallel and antiparallel to the spin direction of the 3d majority electrons, respectively. Correction for $P_c$ was made.

(b) Mn L$_{2,3}$ SXMCD spectrum (bold solid curve) deduced from the XAS spectra in Fig. (a) and its integral over energy (thin solid curve).

The XAS and SXMCD spectra of La$_{0.8}$Sr$_{0.2}$MnO$_3$ and SrFe$_{0.6}$Co$_{0.4}$O$_3$ were found to be qualitatively similar to those of La$_{0.8}$Sr$_{0.2}$MnO$_3$ and SrFe$_{0.6}$Co$_{0.4}$O$_3$, respectively.

It is seen that all the SXMCD spectra exhibit a large negative peak followed by a smaller positive peak around the L$_3$ edge with increasing photon energy. A closer examination shows that the absolute-intensity ratio of the positive to the negative L$_3$ SXMCD peaks is much smaller for the Co L$_3$ edge than for the Mn and Fe L$_3$ edges. It is also found that the SXMCD spectrum of La$_{0.8}$Sr$_{0.2}$MnO$_3$ shows double positive peaks at the Mn L$_2$ edge whereas those of SrFe$_{0.6}$Co$_{0.4}$O$_3$ exhibit a single positive peak at both the Fe and Co L$_2$ edges. The most interesting feature in Figs. 1(b) - 3(b) is that the energy integral of the SXMCD spectrum ∫Δμdω for the Mn and Fe L$_{2,3}$ edges crosses the abscissa with increasing photon energy and takes small values at the upper energy limit.
Fig. 2 (a) Polarization-dependent Fe $L_{2,3}$ XAS spectra of SrFe$_{0.6}$Co$_{0.4}$O$_3$. The solid and dashed curves denote the XAS spectra for the photon helicity parallel and antiparallel to the spin direction of the 3d majority electrons, respectively. Correction for $P_c$ was made. (b) Fe $L_{2,3}$ SXMCD spectrum (bold solid curve) deduced from the XAS spectra in Fig. (a) and its integral over energy (thin solid curve).

whereas that for the Co $L_{2,3}$ edges does not change its sign with increasing energy and takes a large negative value at the upper energy limit.

The SXMCD orbital sum rule$^{19}$ tells that $m_{\text{orb}}$ in the ground state is directly proportional to $\int \Delta \mu \, d\omega$:

$$m_{\text{orb}} = 4 \int_{L3+L2} (\mu_+ - \mu_-) \, d\omega = \frac{10 - n_{3d}}{3} \int_{L3+L2} (\mu_+ + \mu_-) \, d\omega$$  \hspace{1cm} (1)

If the magnetic dipole term is neglected, the SXMCD spin sum rule$^{20}$ is given as

$$m_{\text{spin}} = 2 \int_{L3} (\mu_+ - \mu_-) \, d\omega - 4 \int_{L2} (\mu_+ - \mu_-) \, d\omega = \frac{10 - n_{3d}}{6} \int_{L3+L2} (\mu_+ + \mu_-) \, d\omega$$  \hspace{1cm} (2)

Here $m_{\text{orb}}$ and $m_{\text{spin}}$ are in units of $\mu_B$/atom, $n_{3d}$ is the 3d electron occupation number, and $L_3$ and $L_2$ denote the range of integration. The necessary condition for neglecting the magnetic dipole term is satisfied in the present case, since the 3d electrons in both compounds are under the crystal field of (approximately) octahedral symmetry. It is pointed out here that $\int_{L3} (\mu_+ - \mu_-) \, d\omega$ is negative and $\int_{L2} (\mu_+ - \mu_-) \, d\omega$ is positive for all of the Mn, Fe, and Co $L_{2,3}$ edges, thus yielding a positive $m_{\text{spin}}$ in our definition. It is easily seen from Figs. 2(b) and 3(b) and eqs. (1) and (2) that $m_{\text{orb}}$ of the nominal Fe$^{3+}$ ion with the 3$d^4$ configuration is very small and opposite in sign to $m_{\text{spin}}$, whereas $m_{\text{orb}}$ of the nominal Co$^{4+}$ ion with the 3$d^5$ configuration is large and same in sign with $m_{\text{spin}}$. Similarly, the average $m_{\text{orb}}$ of the nominal Mn$^{3+}$ (80%) and Mn$^{4+}$ (20%) ions is found from Fig. 1(b) to be finite but small with a sign opposite to that of $m_{\text{spin}}$.

We first note that $m_{\text{orb}}$ will be zero for the 3$d^5$ configuration. If this is taken into account, our
observations clearly show that the nominal Co\textsuperscript{4+} ion is not in the 3\textit{d} configuration but in the highly charge-transferred 3\textit{d}\textsubscript{\textit{p}}L configuration arising from the TM 3\textit{d}-O 2p hybridization, and strongly indicate that the nominal Fe\textsuperscript{4+} ion is dominantly in the quite slightly less-than-half charge-transferred 3\textit{d}\textsubscript{\textit{p}}L configuration. Here, \textit{L} denotes the O 2p ligand-hole state. It is also strongly indicated that the nominal Mn\textsuperscript{3+} ion with the 3\textit{d} configuration and Mn\textsuperscript{4+} ion with the 3\textit{p} configuration are dominantly in the highly charge-transfered 3\textit{d}\textsubscript{\textit{p}}L and 3\textit{d}\textsubscript{\textit{p}}L states, respectively. The present result for the nominal Fe\textsuperscript{4+} ion agrees nicely with a reported 3\textit{d} occupation number of \(n_{3d} = 4.85\) for SrFeO\textsubscript{3} (x=0) estimated from comparison of a cluster-model calculation with x-ray photoemission spectra\textsuperscript{26}. The feature of the present Mn \(L_{2,3}\) XMCXD spectrum, particularly the doublet structure at the \(L_{2}\) edge, agrees well with the calculated XMCXD spectrum for the Mn\textsuperscript{2+} ion\textsuperscript{27}; the calculated Mn \(L_{2,3}\) XMCXD spectra for the Mn\textsuperscript{3+} and Mn\textsuperscript{4+} ions exhibit a strong negative peak in the lower energy side of the \(L_{2}\) edge\textsuperscript{28}, which disagrees with the present Mn \(L_{2,3}\) XMCXD spectrum (Fig. 1(b)). These good agreement with reported calculations\textsuperscript{27,28} strongly supports our interpretation of the present XMCXD results.

Knowledge of \(n_{3d}\) is needed for a quantitative determination of \(m_{orb}\). We use here a calculated value of \(n_{3d}(\text{Fe}) = 4.85 \pm 0.15\textsuperscript{26}\) and assumed values of \(n_{3d}(\text{Co}) = 5.8 \pm 0.2\) and \(n_{3d}(\text{Mn}) = 4.5 \pm 0.5\). By subtracting the background simulated by a two-step function from the XAS spectra and integrating the resultant spectra, we obtain from eq.(1) that \(m_{orb}(\text{Mn}) = -0.043 \pm 0.004 \mu_{B}/\text{Mn}, m_{orb}(\text{Fe}) = -0.0080 \pm 0.0003 \mu_{B}/\text{Fe}, and m_{orb}(\text{Co}) = +0.185 - 0.025(+0.005) \mu_{B}/\text{Co}\). The errors arise mainly from the uncertainties in \(n_{3d}\) values for Mn and Fe and from nonsaturation of the integral of XAS for Co in the energy range of the present measurements (an error of -0.025). It is noted that the present \(m_{orb}(\text{Co})\) value is larger than that of metal Co. The present value for the average \(m_{orb}(\text{Mn})\) agrees with a weighted average value estimated using the result of calculations for the Mn\textsuperscript{2+} and Mn\textsuperscript{3+} ions\textsuperscript{28}.

The highly charge-transferred state is not necessarily the unique solution that can explain only the behavior of \(m_{orb}\) deduced from the TM \(L_{2,3}\) XMCXD spectra. The \(t_{2g}^{1}\textsuperscript{3}\) high-spin state usually supposed for the Mn\textsuperscript{4+} ion could give a zero \(m_{orb}\) value, since the \(t_{2g}^{1}\) state is fully occupied. The \(t_{2g}^{1}\textsuperscript{3}e_{g}^{1}\textsuperscript{1}\) high-spin state supposed for the Fe\textsuperscript{3+} or Mn\textsuperscript{4+} ion could also yield a small value of \(m_{orb}\), since an unpaired \(e_{g}\) electron will have no orbital magnetic moment without the spin-orbit interaction.

The XMCXD measurements at the O K edge, in addition to those at the TM \(L_{2,3}\) edges, could more convincingly discriminate between the two possibilities of the charge-transferred and non-charge-transferred states. Pellegrin et al.\textsuperscript{22,23} reported XMCXD spectra around the O K edge in La\textsubscript{2-x}Sr\textsubscript{x}MnO\textsubscript{3} (x=0.18 and 0.4), claiming that their observation gives evidence for an orbital magnetic moment of the O 2p component ferromagnetically coupled to the Mn moments. We have observed a clear XMCXD at the O K edge in SrFe\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3} as well as in La\textsubscript{2-x}Sr\textsubscript{x}MnO\textsubscript{3} by improving the experimental technique such as a higher magnetic field, a lower temperature, the vacuum of the XMCXD chamber, and the sample-surface preparation (not shown here). In particular, an O K XMCXD signal amounting to a value >10% was observed in SrFe\textsubscript{0.6}Co\textsubscript{0.4}O\textsubscript{3}. This O K XMCXD is extraordinarily large for a (non)magnetic element. If there is a strong O 2p-TM 3d hybridization, this should induce a large charge transfer from the O 2p to TM 3d states. The charge transfer could result in strong spin polarization of the O 2p state, thus producing the XMCXD signal at the O K edge. On the contrary, if the TM 3d-O 2p hybridization is negligibly small, no XMCXD effect could be expected at the O K edge, because oxygen is non-magnetic in the normal state. Thus, the observation of the large O K XMCXD shows strong spin polarization of the O 2p state, giving unambiguous evidence for the O 2p-TM 3d hybridization-induced charge-transferred ground state in both compounds. The detailed analysis of the O K XMCXD is under way, the results of which will be presented elsewhere.

4. Conclusions

We have presented the results of XMCXD measurements made around the TM \(L_{2,3}\) core edges in perovskite-type TM oxides La\textsubscript{2-x}Sr\textsubscript{x}MnO\textsubscript{3} and SrFe\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3}. An application of the XMCXD orbital sum rule to the data, together with the observation of the O K XMCXD, has provided experimental evidence for the tacitly accepted picture of the 3d-2p hybridization-induced, highly charge-transferred 3d\textsuperscript{4+}L ground state with \(n\) denoting the nominal 3d electron number in both compounds. The present results agree well with reported calculations for the 3d electron occupation number in SeFeO\textsubscript{3} and for the Mn \(L_{2,3}\) XMCXD spectrum of the Mn\textsuperscript{2+} ion. Our results show that any future theories attempting to fully explain the electrical and magnetic properties of TM oxides should take into account the O 2p ligand-hole state.

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References


