Microscopic origin of ferrimagnetism of a double perovskite Sr₂FeMoO₆: An x-ray magnetic circular dichroism study

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Abstract. We have studied the microscopic magnetic state of a double perovskite Sr₂FeMoO₆ by x-ray magnetic circular dichroism (XMCD). An Fe L₃,₂-edge XMCD reveals that the formal Fe³⁺ ions have an appreciable orbital moment (morb) parallel to their large spin moment (mspin), showing the charge-transfer-induced, minority-spin (↓) Fe t₂g electrons. A weak but undoubted O K-edge XMCD was successfully detected, showing an O 2p-hole morb induced by 2p-3d hybridization. Along with information obtained from the observed Mo M₃,₂-edge XMCD, our findings verify the partially filled Fe 3d t₂g-Or 2pπ-O 2pπ-Mo 4d t₂g hybridized bands at the Fermi level, which mediates ferrimagnetism.

1. Introduction

Tunneling magnetoresistance (TMR) under low fields even at room temperature in ordered double perovskite, Sr₂FeMoO₆ [1], offers the possibility of a new class of magnetoresistive oxides. Despite intrinsically non-magnetic Mo atoms being located between Fe atoms [1], the perovskite has been reported to be a ferrimagnet with the Mo spin antiparallel to the Fe spin [2] and with a high Curie temperature of TC ≥ 400K. The oxide is theoretically predicted to be half metallic, with only the minority-spin (↓) density of states being at the Fermi level (EF) [1]. This nature is thought to be the origin of the TMR effect. These properties are partly similar to those of manganites [3], thereby being expected to provide a key clue to underlying physics of colossal MR in manganites [3]. Despite many studies of Sr₂FeMoO₆, fundamental issues for understanding the origin of its unique magneto-transport properties still remain controversial.

The key issues to be experimentally clarified in Sr₂FeMoO₆ include: (i) What is the real valence or 3d-electron configuration of the nominal Fe³⁺ ions? Do the formal Fe³⁺ ions have a finite orbital magnetic moment (morb) or not?; (ii) Is the O 2p state magnetically polarized? What role and how do the formal O²⁻ ions play in mediating ferrimagnetic interaction? Theories predict the reported ferrimagnetism ascribable to the Mo 4d-Fe 3d hybridization by implicitly considering the O 2p states [4-7]. This effect should induce p-d charge transfers and strongly affect the valence and the mspin and morb values of constituent ions. X-ray magnetic circular dichroism (XMCD) [2, 8], neutron-diffraction [9, 10], and Mössbauer spectroscopy [11, 12] studies have reported contradictory results. Most importantly, no experiment has yet been reported on the O 2p state, though it should play a crucial role in mediating the magnetic interaction. Thus, the issues
on the microscopic electronic and magnetic states of \( \text{Sr}_2\text{FeMoO}_6 \) are yet unsettled. XMCD experiments [13] with sum-rules [14,15] could allow directly approaching the issues through an element-specific, separate determination of \( m_{\text{spin}} \) and \( m_{\text{orb}} \). Here we report on a microscopic study of the element-specific, valence-orbital-selective spin and orbital states of \( \text{Sr}_2\text{FeMoO}_6 \) by high-precision XMCD measurements at the \( \text{Fe} \ L_{3,2} \) and \( \text{O} \ K \) edges, resolving issues (i) and (ii).

2. Experiment
Polycrystalline samples of \( \text{Sr}_2\text{FeMoO}_6 \) were used. The Curie temperature \( (T_C) \) was determined to be \( T_C \approx 430 \text{ K} \) by magnetization measurements. The details of sample growth and characterization were reported elsewhere [1]. XMCD experiments were made by detecting x-ray absorption spectra (XAS) using the total electron-yield method with circularly polarized synchrotron radiation on helical-undulator (AR-NE1B) and bending-magnet (BL-11A) beam lines at the Photon Factory. The sample temperature was \( \approx 10-30 \text{ K} \) much lower than \( T_C \). The sample surface was diamond-filed \textit{in-situ} in a preparation chamber. Magnetic fields of \( B = \pm (1.1-2.5) \text{T} \) were applied to the sample parallel and antiparallel to the photon helicity \( (h) \) using a superconducting magnet [16] and a permanent-magnet flipper-type XMCD apparatus. The field direction was switched with \( h \) fixed on BL-11A. With the flipper on NE1B, the field was reversed at every photon energy without any derivative-like XMCD artifact, and the \( h \) was also reversed. The degree of circular polarization \( (P_C) \) was evaluated to be \( \pm 95 \pm 3 \% \) on NE1B and chosen to be \( +78 \pm 3\% \) on BL-11A [13].

3. Results and discussion
Figures 1(a) and 1(b) show polarization-dependent \( \text{Fe} L_{3,2} \)-edge XAS (\( \mu_+ \) and \( \mu_- \)) and \( P_C \)-corrected XMCD (\( \Delta \mu = \mu_+ - \mu_- \)) taken at \( T \approx 30 \text{ K} \) under \( B = \pm 2.5 \text{ T} \). The energy integrated XMCD is also displayed in Fig.1(b). A linear background has been subtracted in XAS. Here \( \mu_+ \) and \( \mu_- \) stand for the absorption coefficients with \( h \) parallel and antiparallel to the \( \text{Fe} \ 3d \) majority-spin (\( \uparrow \)) direction. A strong XMCD was

![Figure 1](image1.png)

**Figure 1** (a) Polarization-dependent XAS and (b) XMCD (solid) and its energy-integrated (dashed) spectra at the \( \text{Fe} L_{3,2} \) edges in \( \text{Sr}_2\text{FeMoO}_6 \). The spectra were taken at \( T = 30 \text{ K} \) and \( B = \pm 2.5 \text{ T} \). A linear background has been subtracted in (a). Correction for \( P_C \) has been made in (a) and (b). A normalization was made in (a) such that the sum of the \( L_3 \) XAS peaks was equal to 200.

![Figure 2](image2.png)

**Figure 2** (a) Polarization-dependent XAS and (b) XMCD (green and blue curves) and its energy-integrated (red curve) spectra at the \( \text{O} K \) edge in \( \text{Sr}_2\text{FeMoO}_6 \). The spectra were taken at \( T = 20 \text{ K} \) and \( B = \pm 1.1 \text{ T} \). The XMCD spectrum taken by a reversal of \( h \) (blue curve: \( \Delta \mu = \mu_+ - \mu_- \)) is displayed for comparison. A linear background has been subtracted in (a). Correction for \( P_C \) has been made.
observed at the Fe L$_{3,2}$ edges, which indicates the high-spin state of the Fe ion. In addition, our analytical result, $\Delta A_i + \Delta A_j < 0$, shows that $m_{\text{orb}}(\text{Fe}) (> 0)$ is appreciable and parallel to $m_{\text{spin}}(\text{Fe}) (> 0)$ on the basis of the XMCD orbital sum rule [14]. This result is in sharp contrast with the previous XMCD studies [2, 8] which reported that $\Delta A_i + \Delta A_j = 0$, i.e., $m_{\text{orb}}(\text{Fe}) \approx 0$, being important for elucidating the electronic states of Sr$_2$FeMoO$_6$. Since the nominal high-spin Fe$^{3+}$ ion should take the $t_{2g}[^3e_g]^{2}t_{2g}[^3t_2g]^{3}$ configuration with a vanishing $m_{\text{orb}}$, the present result demonstrates the existence of the charge-transfer-induced Fe 3d $t_{2g}[^3t_2g]$ electrons. We thus conclude that the Fe ion is in the O 2p$_{\uparrow}$-to-Fe 3d$\downarrow$ charge-transfered (δ > 0), more-than-half, Fe$^{3+}$-$t_{2g}[^3t_2g]^{3}t_{2g}[^3e_g]^{2}$ configuration. This result is consistent with the Mössbauer result [11,12]. Although there is a possibility of coexistence of the charge-transfered state and the mixed-valence state, the resolution of the present measurements is not high enough for judging it from the line shape.

Figure 2 shows the polarization-dependent O K-edge XAS and $P_{\text{C}}$-corrected XMCD in the first XAS sharp-peak region. The measurements were made at $T \approx 20$ K and for $B = \pm 1.1$ T. Green and blue curves in Fig. 2(b) represent $\Delta \mu (= \mu_\uparrow - \mu_\downarrow)$ and $-\Delta \mu (= \mu_\downarrow - \mu_\uparrow)$, respectively, taken by reversing the helicity ($h$) of helical undulator radiation. Although $\mu_\uparrow$ and $\mu_\downarrow$ in Fig. 2(a) show no appreciable difference, a small but undoubted XMCD was successfully observed and confirmed by its sign reversal on reversing $h$ in addition to the flipper’s assurance of no differential XMCD artifact.

The O K-edge XAS shows the existence of O 2p holes. The result that $\int \Delta \mu(t) < 0$ demonstrates the magnetic polarization of the O 2p holes with a finite $m_{\text{orb}}(\text{O}) (> 0)$ which is parallel to $m_{\text{spin}}(\text{Fe}) (> 0)$ by the orbital sum rule [14]. From the fact that $m_{\text{orb}}(\text{Fe}) (> 0)$ and $m_{\text{orb}}(\text{O}) (> 0)$, we infer that the observed $m_{\text{orb}}$ should be induced by 2p-3d hybridization and a resultant 2p-to-3d charge transfer. The O K-edge XMCD gives no information about $m_{\text{spin}}(\text{O})$ because of the absence of spin-orbit (SO) interaction in the O 1s core hole. However, the O 2p$_{\downarrow}$-to-Fe 3d$\downarrow$ charge transfer indicates that the holes should reside in the O 2p$_{\downarrow}$ state with a resulting net up-spin (↑) polarization of the O 2p level, i.e., $m_{\text{spin}}(\text{O}) > 0$ with the sign definition of $m_{\text{spin}} > 0$ for $S_\text{z} > 0$. The substantial O K-edge XMCD (−2%) indicates that $m_{\text{orb}}(\text{O})$ should arise from the orbital current directly transferred from $m_{\text{orb}}(\text{Fe})$ via the Fe 3d $t_{2g}[^3t_2g]^{3}O 2p_{\downarrow}$ wave-function overlap but cannot be ascribed to the two-step mechanism by the O 2p-hole SO interaction under hybridization-induced 2p spin polarization.

We now determine $m_{\text{spin}}$ and $m_{\text{orb}}$ using the XMCD sum rules [14,15]. The orbital [14] and angle-averaged spin [15,17] sum rules are given for the L$_{3,2}$ and M$_{3,2}$ edges by

$$m_{\text{orb}} = -\frac{4}{3} \frac{\Delta A_i + \Delta A_j}{A_i + A_j} n_k,$$

$$m_{\text{spin}} = -\frac{2}{3} \sum_{\alpha=x,y,z} \frac{2\Delta A_j}{(A_i + A_j)^2} n_{\alpha},$$

where $m_{\text{orb}}$ and $m_{\text{spin}}$ are in units of $\mu_B$/atom, $n_k$ is the 3d or 4d hole number, $\Delta A_i$ and $A_i$ (j = L, M; k = 2, 3) are the j$\alpha$-edge-integrated XMCD and XAS intensities, respectively. For the present polycrystalline sample, $m_{\text{spin}}$ can be directly determined using the angle-averaged spin sum rule (2) with allowed neglect of the magnetic dipole moment [17]. We shall employ for $m_{\text{spin}}$ a correction factor (C.F.) given by theory [18] that takes into account the Coulomb interaction between electrons based on the full atomic multiplet and $O_h$ crystal field. Using a 3d hole number of $n_h(3d) = 4.4 \pm 0.3$ ($\delta = 0.6 \pm 0.3$) supported by Mössbauer spectroscopy studies [11,12] and a C.F. as averaged from theoretical ones for the Fe$^{3+}$ and Fe$^{2+}$ high-spin ions [18], we obtain $m_{\text{spin}}(\text{Fe}) = 2.80 \pm 0.30 \mu_B$, $m_{\text{orb}}(\text{Fe}) = 0.093 \pm 0.01 \mu_B$, and $m_{\text{orb}}(\text{Fe}) = 2.89 \pm 0.30 \mu_B$.

We have observed the XAS and XMCD at the Mo M$_{3,2}$ edges (not shown here). For Mo, we first determine the ratio of the orbital to spin moments. Relying only on the Mo-edge XMCD integral, we get $m_{\text{orb}}(\text{Mo})/m_{\text{spin}}(\text{Mo}) = -0.105 \pm 0.020$. Using a zeroth-order 4d hole number, $n_h(4d) = 9.0$, we obtain $m_{\text{spin}}(\text{Mo}) = +0.36 \pm 0.03 \mu_B$, $m_{\text{orb}}(\text{Mo}) = +0.037 \pm 0.015 \mu_B$, and $m_{\text{orb}}(\text{Mo}) = -0.32 \pm 0.03 \mu_B$. The nonzero $m_{\text{orb}}(\text{Mo})$ which is antiparallel to $m_{\text{spin}}(\text{Mo})$ is reasonable for the present less-than-half Mo system.

We next estimate $m_{\text{orb}}(O)$. The XAS and XMCD at the Mo M$_{3,2}$ edges are much weaker than those at the Fe L$_{3,2}$ edges. This fact indicates that the contribution to the O K-edge XAS and XMCD of the Mo 4d
states via $2p$-$4d$ hybridization is negligibly small even for charge transfer ($\delta'$ $\neq 0$ compared with that of the Fe 3$d$ states through $2p$-$3d$ hybridization. Hence, approximating the O 2$p$ hole number, $n_{O}(O)$, to that arising only from the $2p$-to-$3d$ charge transfer ($\delta$ $\approx 0.6$) leads to $n_{O}(O) = 0.6 \approx 0.1$. This gives an estimate of $m_{\text{orb}}(O)$ from the XMCD using the K-edge orbital sum rule as $m_{\text{orb}}(O) = -2/3 \cdot (\Delta_{K}/\Delta_{L}) \cdot n_{O}(O) \approx (0.3 \pm 0.1) \times 10^{-3} \mu_{B}$, where $\Delta_{K}$ and $\Delta_{L}$ are the XMCD and XAS energy integrals at the O K edge. This value is as small as 1.5% of $n_{O}(O)$ $\approx 0.02 \mu_{B}$ in SrFeCoO$_{3}$ [19], where the O 2$p$-Fe, Co 3$d$ hybridization and the resultant XMCD are gigantic. In contrast to $m_{\text{orb}}(O)$, $m_{\text{spin}}(O)$ is difficult to estimate, since an accurate $n_{O}(O)$ value is unknown and $m_{\text{spin}}(O)$ does not contribute to the O K-edge XMCD. However, the existence of holes in the down spin indicates the O 2$p$ spin polarization, $m_{\text{spin}}(O) > 0$. Neglecting $m_{\text{spin}}(O)$ and $n_{O}(O)$, we get $m_{\text{tot}} \approx m_{\text{tot}}(Fe) + m_{\text{tot}}(Mo) \approx 2.57 \pm 0.20 \mu_{B}$. The XMCD-derived $m_{\text{tot}}$ value of the system agrees with a magnetization-derived $m_{\text{tot}}$ value of 3.0 $\mu_{B}$ [1].

The present $m_{\text{tot}}(Fe)$ agrees with theories [5,6] and Mössbauer-spectroscopy studies [11,12] which claimed the intermediate Fe$^{2+}$ valence for the nominal Fe$^{3+}$ ions. The result that $m_{\text{spin}}(Fe) > 0$, $m_{\text{spin}}(O) > 0$, and $m_{\text{spin}}(Mo) < 0$ shows that the nominal O$^{2-}$ ion makes a ferromagnetic interaction with the formal Fe$^{3+}$ ions and an antiferromagnetic interaction with the Mo$^{5+}$ ions, leading to total ferrimagnetic order. Our results negate the results of previous XMCD studies [2,8], which reported an undetectable O K-edge XMCD, a very small $m_{\text{tot}}(Fe)$ or even a small negative $m_{\text{tot}}(Fe)$ ($= -0.036 \mu_{B}$), antiparallel to $m_{\text{spin}}(Fe)$, despite for the more-than-half system.

We give here a schematic picture of the element-specific, spin-dependent density of states and of the representative Fe 3$d_{xy}$ $t_{2g\downarrow}$-O 2$p_{z}$-Mo 4$d_{xy}$ $t_{2g\downarrow}$ hybridized states near $E_{F}$, which is deduced from the present observations. Our results show that unpaired electrons exist in the Fe 3$d$ $t_{2g\downarrow}$-O 2$p_{z}$-Mo 4$d_{xy}$ $t_{2g\downarrow}$ hybridized bands crossing $E_{F}$ and that the magnetically polarized O 2$p$ states should play an essential role in mediating ferrimagnetic interaction. This finding is crucial for uncovering the magnetic and electronic states of Sr$_{2}$FeMoO$_{6}$, since the O 2$p$-Fe, Co 3$d$ hybridization and the resultant XMCD are gigantic. In contrast to $m_{\text{orb}}(O)$, $m_{\text{spin}}(O)$ is difficult to estimate, since an accurate $n_{O}(O)$ value is unknown and $m_{\text{spin}}(O)$ does not contribute to the O K-edge XMCD. However, the existence of holes in the down spin indicates the O 2$p$ spin polarization, $m_{\text{spin}}(O) > 0$. Neglecting $m_{\text{spin}}(O)$ and $n_{O}(O)$, we get $m_{\text{tot}} \approx m_{\text{tot}}(Fe) + m_{\text{tot}}(Mo) \approx 2.57 \pm 0.20 \mu_{B}$. The XMCD-derived $m_{\text{tot}}$ value of the system agrees with a magnetization-derived $m_{\text{tot}}$ value of 3.0 $\mu_{B}$ [1].

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4. Conclusion

We have presented evidence for substantial $m_{\text{tot}}(Fe)$ and $m_{\text{tot}}(O)$ which are parallel to $m_{\text{spin}}(Fe)$ in Sr$_{2}$FeMoO$_{6}$. We have observed finite antiparallel $m_{\text{spin}}(Mo)$ and $m_{\text{tot}}(Mo)$, the former being antiparallel to $m_{\text{spin}}(Fe)$. Combined information of these quantities resolve controversial issues (i)-(ii), verifying theoretically predicted Fe 3$d$ $t_{2g\downarrow}$-O 2$p_{z}$-Mo 4$d$ $t_{2g\downarrow}$ hybridized bands across $E_{F}$. The present $m_{\text{tot}}(Fe)$ agrees with theories [5,6] and Mössbauer-spectroscopy studies [11,12] which claimed the intermediate Fe$^{2+}$ valence for the nominal Fe$^{3+}$ ions. The result that $m_{\text{spin}}(Fe) > 0$, $m_{\text{spin}}(O) > 0$, and $m_{\text{spin}}(Mo) < 0$ shows that the nominal O$^{2-}$ ion makes a ferromagnetic interaction with the formal Fe$^{3+}$ ions and an antiferromagnetic interaction with the Mo$^{5+}$ ions, leading to total ferrimagnetic order. Our results negate the results of previous XMCD studies [2,8], which reported an undetectable O K-edge XMCD, a very small $m_{\text{tot}}(Fe)$ or even a small negative $m_{\text{tot}}(Fe)$ ($= -0.036 \mu_{B}$), antiparallel to $m_{\text{spin}}(Fe)$, despite for the more-than-half system.

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