Electronic and magnetic structures of Sr$_2$FeMoO$_6$

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We have investigated the electronic and magnetic structures of Sr$_2$FeMoO$_6$ employing site-specific direct probes, namely x-ray absorption spectroscopy with linearly and circularly polarized photons. In contrast to some previous suggestions, the results clearly establish that Fe is in the formal trivalent state in this compound. With the help of circularly polarized light, it is unambiguously shown that the moment at the Mo sites is below the limit of detection (< 0.25 $\mu_B$), resolving a previous controversy. We also show that the decrease of the observed moment in magnetization measurements from the theoretically expected value is driven by the presence of mis-site disorder between Fe and Mo sites.

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The observation of colossal magnetoresistance (CMR) in the perovskite mixed valent manganites has led to a renewed interest in ferromagnetic oxides. It is believed that the double exchange mechanism in presence of strong electron-phonon couplings arising from Jahn-Teller distortions is responsible for the observed properties in the manganites [1]. Recently, double perovskite Sr$_2$FeMoO$_6$ was established as a new CMR material [2]. This compound, in contrast to the manganites, has certain technologically desirable properties, such as a substantial MR at a low applied field even at the room temperature. From a fundamental point of view, it is even more important to note that crystallographic data does not indicate any JT distortion and the lattice does not appear to play any significant role in this compound. Furthermore, the system is an undoped one in contrast to the manganites. Thus, Sr$_2$FeMoO$_6$ is in principle a simpler system to understand its properties in detailed theoretical terms. In spite of this apparent simplicity, there are surprisingly many open issues concerning the basic electronic and magnetic structures of this compound.

In this compound, each of the Fe$^{3+}$ ($S = 5/2$) and Mo$^{5+}$ ($S = 1/2$) sublattices are believed to be arranged ferromagnetically, while the two sublattices are coupled to each other antiferromagnetically. It has been suggested [2] that the system is in a half metallic ferrimagnetic (HMFM) state leading to its fascinating CMR properties. However, there appears to be several controversies concerning the real nature of this compound. One neutron diffraction study [3] reported the absence of any moment at the Mo sites, suggesting Mo to be essentially nonmagnetic, whereas another study [4] suggested $\sim 1 \mu_B$ at each Mo site. Moreover, analysis of Mössbauer results have been interpreted both in terms of Fe$^{3+}$ [5] and Fe$^{2.5+}$ [6] states. Thus, it is obvious that even the basic issues concerning the electronic and magnetic structures of this compound have not been settled so far. Since the analysis of neutron and Mössbauer data are model dependent, it is obviously necessary to obtain site-specific direct information concerning the electronic and magnetic properties of this compound. Additionally, in the originally proposed magnetic structure [2], the system is expected to have a moment of 4 $\mu_B$ per formula unit (f.u.) due to the ferrimagnetic coupling between the Fe$^{3+}$ 3$d^5$ and Mo$^{5+}$ 4$d^1$ configurations. However, the observed saturation magnetization ($M_S$) is often found [5,6] to be about 3 $\mu_B$/f.u. The origin of this reduction in the magnetic moment is also not clear at present. We address all these issues combining linear and circularly polarized x-ray absorption spectroscopy (XAS), with its ability to provide direct, site-specific electronic and magnetic informations. In addition to providing the magnetic structure of this compound and explaining the reduction in the observed moment, our results also suggest that this compound cannot be described within the conventional double exchange mechanism.

Sr$_2$FeMoO$_6$ can exist with varying extent of mis-site disorder between the Fe and Mo sublattices. Synthesis and characterization of highly ordered ($\sim 90\%$) and extensively disordered (ordering of $\sim 30\%$) Sr$_2$FeMoO$_6$ have been described in our earlier publication [2]. The experiments were carried out at the 4.2R circularly polarized beamline at Elettra Synchrotron Radiation Facility. The measurements were performed at 77 K, which is well below the magnetic ordering temperature ($\sim 420$ K) [6]. The sample surface was cleaned in situ by scraping with a diamond file. The degree of circular polarization at the relevant photon energy was approximately 85%.

In order to address the valence state of Fe in such oxides, it is most suitable to probe the Fe 2$p_{3/2}$ ($L_3$) XAS which exhibits very clear differences between formal Fe$^{2+}$ and Fe$^{3+}$ states. Specifically, the 2$p_{3/2}$ absorption edge of all Fe$^{2+}$ species in an octahedral crystal field exhibits a main peak at a lower energy, followed by a weaker peak or shoulder at a higher energy. The ordering of the peaks is reversed for Fe$^{3+}$ species [11] providing an easy way to identify the formal Fe valence state independent of the
extent of covalency. We have recorded a high resolution
\((\sim 0.3 \text{ eV})\) Fe 2p_{1/2} absorption spectrum of Sr₂FeMoO₆
with linearly polarized light (Fig. 1). From this figure, it is
evident, even in absence of any detailed analysis that only a Fe³⁺
valence state is consistent with the experimental result, exhibiting
a weaker lower energy shoulder and a higher energy main peak.
However, in order to provide a quantitative description of the spectral
features and, more importantly, of the ground state, it is important
to carry out detailed calculations including hybridization effects with
the ligands within a cluster model on an equal footing as core-valence and valence-valence
multiplet interactions and crystal-field effects, as the participation
of the ligand levels in determining the spectral features may be significant.[12]
In order to minimize the number of free parameters, we fix the multiplet interaction
strengths, \(F_{dd}^{2p} \) (9.7 eV), \(F_{dd}^{2d} \) (6.1 eV), \(F_{pd}^{2p} \) (5.4 eV),
\(G_{pd}^{3p} \) (3.9 eV), and \(G_{pd}^{3d} \) (2.2 eV) to 80% of the atomic
Hartree-Fock values to account for the solid state screening.
Additionally, the hopping parameter strengths, \(pσ, pδσ, \) and \(pσσ\) of -1.7, 0.9 and 0.45 eV, respectively, are
guided by a tight-binding fitting[13] of the spin-polarized
\(ab \ initio\) band dispersions. Moreover, we fix the multi-
plet averaged 2p core - 3d valence Coulomb interaction
strength, \(U_{pd}\), to be 1.2 times that of \(U_{dd}\) between the
3d electrons, according to the usual practice. Thus, we are left with only two adjustable parameters, namely \(U_{dd}\)
and the 2p - Fe 3d charge transfer energy, \(\Delta\). Since
the resulting many-body problem within a complete basis
approach[12] involves nearly 30,000 basis states, the calculations were carried out within the Lanczos algo-

rithm. We obtain a remarkably good description of the spectral features with \(U_{dd} = 4 \text{ eV}\) and \(\Delta = 3 \text{ eV}\) for the Fe³⁺
configuration, as shown in Fig. 1. \(U_{dd}\) and \(\Delta\) esti-
mated here are consistent with those in other octahedral
Fe³⁺ oxides. The many-body ground state has 60.2% \(d^9\),
34.5% \(d^6 \underline{L}^1\) and 5.1% \(d^7 \underline{L}^2\) character, suggesting the system
to be somewhat more ionic than even LaFeO₃[14].

It should be noted here that it was not possible to describe
the spectral features at all starting with a formal Fe²⁺
configuration and then including configuration interaction
for any choice of parameter strengths, conclusively establishing
the 3+ valence state of Fe in Sr₂FeMoO₆.

While the XAS with linearly polarized light at the
Fe 2p edge provides a definitive description of the site-
specific electronic structure, it is not as specific to the
magnetic structure as x-ray magnetic circular dichroism
(XMCD) results would be. In order to specifically investi-
gate the magnetic structure, we have carried out XAS
at the Fe 2p and Mo 3p edges with circularly polarized
light. We use a lower resolution (\(\sim 1.0 \text{ eV}\) at the Fe 2p
edge) to improve substantially the signal-to-noise ratio,
though this smoothens out the detailed spectral features
which are very similar to those with linearly polarized
light (Fig. 1). In Fig. 2(a), we show the photon-flux
normalized polarization-dependent Fe 2p XAS spectra,
\(\mu^+\) and \(\mu^-\) for highly ordered Sr₂FeMoO₆, correspond-
ing to the helicity parallel and anti-parallel to the Fe 3d
majority-spin direction, respectively. The XMCD spec-
tra, \(\Delta \mu = \mu^+ - \mu^-\), also shown in the same panel, clearly
shows a substantial magnetic signal, indicative of a large
Fe moment. The corresponding experimental \(\mu^+, \mu^-\) and
\(\Delta \mu\) spectra for Mo 3p edge are shown in Fig. 2(b). It is
evident from the XMCD spectrum of Mo that any mag-
netic moment at these sites is below the detection limit
(\(< 0.25 \mu_B\)). The present result is in clear contradiction
with the suggestion of a measurable moment (\(\sim 1 \mu_B\))
at the Mo sites[2], while it is in agreement with a previous neutron diffraction measurement[3] where no moment
could be detected at the Mo sites.

The above results, in conjunction with already known
properties of Sr₂FeMoO₆, provide an understanding of the
magnetic structure. The XMCD spectra establish a large
moment at the Fe site, while negating the possibil-
ity of a substantial moment at the Mo sites. However, the
electronic structure of this compound with a formal Fe³⁺
state requires the existence of another electron, nomi-
nally associated with a Mo⁵⁺ 4d⁴ configuration and being
responsible for the metallic behavior. Our results estab-
lish that the spin density arising from this single electron
is not substantially at the Mo site. Since this electron is
delocalized, it is not unreasonable to expect that the
wavefunction of the electron will be spread over several
sites. Band structure results, based on spin-polarized
LMTO-GGA calculations[15] in fact clearly show that the
states at the \(E_F\) are almost equally contributed by
Fe 3d, Mo 4d and O 2p states, suggesting an average of
\(~ 0.3 \mu_B\) down-spin density at each Fe, Mo and six oxy-
gen sites. The present experimental result at the Mo 3p
dge suggests that the spin-density is in reality further re-
duced (\(< 0.25 \mu_B\)) at the Mo sites, compared to the sin-
gle particle calculations. Thus, it appears that the FeO₆
octahedron carry more than 0.75 \mu_B down-spin density,
rather than \(~ 0.6 \mu_B\) suggested by the band structure
results. The suggestion of a substantial down-spin moment
contribution at the Fe site is supported by our many-
body cluster calculations (see Fig. 1), where the ground
state wavefunction is found to have an average down-spin
\(d\) occupancy of 0.45, somewhat larger than that suggested
by the band structure results. Combining all these evi-
dences, it would appear that the delocalized electron spin
density is transferred from the minority spin of the Mo-
sites via hybridization to Fe \(~ 45\%) and O \(\geq 30\%\)
with less than about 25% of spin-density at the Mo site,
thereby spreading over several sites. Thus, it appears
that the delocalized spin density, antiferromagnetically
coupled to the localized up spins at the Fe sites, prefers
to be spatially closer to the central Fe sites, thereby gain-
ing a stronger antiferromagnetic coupling[16] between
the localized and the delocalized spins rather than resid-
ing at the farther Mo sites. While the double exchange
mechanism, applicable to the manganites, has often been invoked to describe these ordered double perovskite systems, the present results clearly suggest a new physics for this class of compounds compared to manganites. In the DE mechanism, the localized spin at the Mn site and the delocalized electrons, largely residing at the same atomic site, are coupled ferromagnetically. In contrast, the present system is reminiscent of previously discussed Zhang-Rice singlet formation in the context of high $T_C$ cuprates \[20\]. In that case the localized moment at the central Cu site is coupled antiferromagnetically with the dopel delocalized spin-density spread over the central Cu and the nearest neighbor oxygen sites to form a singlet state. In the present case, the localized Fe $S = 5/2$ state couples antiferromagnetically with the spin density of delocalized $S = 1/2$ state to form a singlet state. In the present case, the localized Fe $S = 5/2$ state couples antiferromagnetically with the spin density of delocalized $S = 1/2$ state to form a $S = 2$ state.

Having established the basic magnetic structure of Sr$_2$FeMoO$_6$, we now address the issue of consistently observing a lower $M_S$ value for this compound than is expected on the basis of the simple ionic picture, in all reported results. In this context, it is important to note that Sr$_2$FeMoO$_6$ always appears with a finite concentration of mis-site disorder where a pair of Fe and Mo exchange their crystallographic positions. The best compounds have been reported to have $\sim 90\%$ ordering of the Fe and the Mo sites \[21\]. In order to investigate whether such a mis-site disorder can be responsible for the observed reduction of the moment from the ideal value of 4 to about 3 $\mu_B$ and whether the reduction in the total magnetization is related to a corresponding loss in the local magnetic moment of Fe, we have also recorded the XAS at the Fe 2$p$ edge of the extensively disordered Sr$_2$FeMoO$_6$ with circularly polarized light. These edges along with the XMCD result at Fe 2$p$ edges for the disordered sample are shown in Fig. 3(a), while in Fig. 3(b), we compare the XMCD signals from the ordered and disordered Sr$_2$FeMoO$_6$. It is evident from the spectra that the magnetic moment on individual Fe ions decreases remarkably with decreasing ordering. In order to quantify our results, we have calculated the orbital, spin and total moments at the Fe sites from these spectra with the assumption of negligible magnetic-dipole moment, using the well established sum rules \[8,9\]. All the individual spin, orbital and total moments of these two samples are shown in Table 1. In these cases, we find that $m_{orb}$ is very small, due to the approximately 3$\delta$ configuration of Fe ions. The resulting total moments estimated from the XMCD signals are 1.68 and 1.36 $\mu_B$/Fe for the ordered and the disordered systems, respectively. It is to be noted that the magnetic moments obtained from the XMCD results are considerably smaller than the total magnetic moments obtained from bulk magnetization measurements \[22\]. Such discrepancies are well known in the literature \[23\], and may arise from many factors. It has been variously attributed to uncertainties in data analysis, limitations of the applicability of the atomic sum rules arising from non-ideal geometry in real experiments and/or solid-state effects, and non-saturation of the magnetization at modest magnetic fields near the surface region. Thus, the absolute value of the moment estimated from the XMCD results is per se not a useful quantity, though the extensive XMCD literature shows that relative changes in the magnetic moments estimated from XMCD is a very reliable quantity. For our purpose, we first establish this point explicitly by comparing the XMCD results (Fig. 3 inset) of the ordered Sr$_2$FeMoO$_6$ with a bulk magnetic moment of $\sim 2.81$ $\mu_B$/f.u. at 77 K and a closely related compound, Sr$_2$FeMo$_{0.3}$W$_{0.7}$O$_6$, with a bulk magnetic moment of 3.64 $\mu_B$/f.u. at 77 K. The XMCD results (Table 1) measured at the same temperature clearly suggest an approximately 42$\pm$2$\%$ drop in the XMCD moment compared to the bulk one for both the samples. Thus, having established the efficacy of probing the relative changes of magnetization in these and related systems employing XMCD, our results on the ordered and disordered Sr$_2$FeMoO$_6$, shown in Fig. 3 and Table 1, clearly establish a remarkable decrease in the magnetic moment at the Fe sites with increasing mis-site disorder. These experimental results are also consistent with the recent band structure calculations \[13\] within a supercell for mis-site disorder between the Fe and Mo occupancies. The band structure results suggest that a complete disorder would result in a 34$\%$ decrease in the moment at the Fe sites, while a 50$\%$ order would have a 21$\%$ decrease of the moment compared to the fully ordered sample. The present experimental result of a 23$\%$ decrease in the Fe moment for the “disordered” sample with about 30$\%$ ordering is consistent with these band structure results. Thus, it appears that the decrease in the magnetic moment invariably observed for the so-called ordered Sr$_2$FeMoO$_6$ is mainly due to the presence of finite ($\sim 10\%$) mis-site disorder. The origin of the decrease in the Fe moment in presence of mis-site disorder is essentially due to the destruction of the half-metallic ferromagnetic state of the fully-ordered ideal system, thereby transferring $d$-electrons from the up-spin to the down-spin bands \[13\].

In summary, site-specific x-ray absorption spectroscopy with linearly polarized light established the formal valency of Fe in Sr$_2$FeMoO$_6$ to be $3^+$. Detailed investigation of x-ray magnetic circular dichroism data confirms a large moment at the Fe site. Our results provide a direct evidence for a negligible ($< 0.25 \mu_B$) magnetic moment at the Mo site, thereby suggesting that the delocalized electron spin density, coupled antiferromagnetically to the localized Fe-spins, is delocalized over several sites including the neighboring FeO$_6$ octahedra and indicating a novel origin of magnetism, different from the conventional double exchange mechanism. A comparison of XMCD results from the ordered and the disordered samples establishes that the presence of mis-site disorder
between the Fe and Mo sites even in the so-called ordered samples is responsible for the observed drop in the magnetic moment from the expected value of 4 $\mu_B$/f.u. to experimentally observed value of about 3 $\mu_B$/f.u.

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Table 1. Spin moments, Orbital moments and Total moments in $\mu_B$/Fe at 77 K.

| Compound          | $M_{spin}$ | $M_{orb}$       | $M_{tot}$   |
|-------------------|------------|-----------------|-------------|
| Ordered Sr$_2$FeMoO$_6$ | 1.71       | $-3.6 \times 10^{-2}$ | 1.68        |
| Disordered Sr$_2$FeMoO$_6$ | 1.44       | $-7.6 \times 10^{-2}$ | 1.36        |

FIG. 1. Experimental and calculated Fe 2p$_{3/2}$ x-ray absorption spectrum for ordered Sr$_2$FeMoO$_6$.

FIG. 2. x-ray absorption spectra at (a) Fe 2p, and (b) Mo 3p edges for ordered Sr$_2$FeMoO$_6$, measured using circularly polarized light. In the lower panels, circular dichroism signals, the difference between the absorption for right and left circularly polarized light at these edges are shown. The integral difference spectrum for Fe 2p edge is also shown in the lower panel of (a).

FIG. 3. (a) x-ray absorption spectra at Fe 2p-edge for disordered Sr$_2$FeMoO$_6$, measured using circularly polarized light and the corresponding XMCD signal. (b) XMCD signals for the ordered and disordered Sr$_2$FeMoO$_6$. In the inset, the XMCD signals for ordered Sr$_2$FeMoO$_6$ and Sr$_2$FeMo$_{0.3}$W$_{0.7}$O$_6$ are shown.
Fig. 1

Fe $2p_{3/2}$
XAS

Experimental
Calculated
Fig. 2

(a) Fe 2p

Intensity (arb. units)

hν (eV)

(b) Mo 3p

Intensity (arb. units)

hν (eV)
Fig. 3

(a) Fe 2p

(b) XMCD

Intensity (arb. units)

hv (eV)