

Mn K-Edge XMCD Study of the Mixed-Valence State of Mn-Based Molecular Nanomagnets

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Abstract. X-ray Magnetic Circular Dichroism (XMCD) measurements of the Mn_{12}Ac and Mn_4OAc molecular magnets compared with several manganites, such as $\text{LaMn}_{0.5}\text{Ga}_{0.5}\text{O}_3$ (Mn^{3+} reference), $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ (Mn^{4+} reference) and the magnetoresistive $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ are reported. The Mn K edge XAS and XMCD spectra have been measured on powder samples at a fixed temperature of 5 K and with an applied magnetic field of 5T. Weak dichroic signals are observed around the absorption edge in all the samples. XMCD spectra for the three bulk manganites are nearly identical except for the chemical shift to higher energies due to the increase of the formal Mn valence state (~ 3 eV between the Mn^{3+} and Mn^{4+} references). When comparing with the XMCD signals of the molecular magnets, the overall shape is qualitatively similar but the negative peak just on the edge decreases in intensity and becomes larger in width. These results are analyzed from the point of view of the Mn mixed-valence electronic state, which suggest the contribution of two dichroic signals correspondent to the presence of two electronic configurations for the Mn atoms in the case of the molecular magnets.

Keywords: X-ray magnetic circular dichroism, Mn K edge, Mn-based molecular magnets, manganites, electronic state.

PACS: 75.47.Lx, 75.50.Xx, 78.70.Dm, 61.10.Ht

INTRODUCTION

Molecular crystals such as $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ (in short Mn_{12}Ac) [1] and $\text{Mn}_4\text{O}_3(\text{OAc})_4(\text{dbm})_3$ (in short Mn_4OAc) [2] are the subject of an on-going research because of their unusual low-temperature magnetic properties. Of interest is the knowledge of the internal magnetic structure of these molecular magnets. In a simple ionic picture, the magnetic core of the Mn_{12}Ac molecule consists of an internal tetrahedron of four Mn ions, assigned to a $S=3/2$ Mn^{4+} state and an external ring of eight Mn ions, which are in the $S=2$ Mn^{3+} state, leading to an average oxidation state of 3.34 per Mn atom. The Mn_4OAc molecule shows a distorted-cubane core of four Mn ions, one Mn^{4+} and three Mn^{3+} , which results in an average oxidation state of 3.25 per Mn atom. Magnetic susceptibility measurements indicated that the coupling between the Mn^{3+} ions is ferromagnetic, whereas the Mn^{4+} ions couple antiferromagnetically to the Mn^{3+} ones, forming ferrimagnetic clusters of effective spin $S=10$ (Mn_{12}Ac) and $S=9/2$ (Mn_4OAc) at sufficiently low temperatures. Later polarized neutron diffraction experiments on the Mn_{12}Ac [3] deduced different

magnetic moments for the Mn sites at the internal tetrahedron and the outer ring, in agreement with the proposed ionic picture. However, the resulted individual moments were reduced compared to those due to the spin of free Mn^{3+} or Mn^{4+} ions.

The role of the formal mixed-valence Mn-electronic state is fundamental for determining the mechanisms driving the magnetic interactions. XMCD is a powerful tool for investigating electronic states of magnetic atoms due to its element-selectivity, electron shell-specificity and angular momentum sensitivity. Previous XANES and XMCD spectra at the Mn K edge of bulk magnetoresistive manganites [4], with similar formal mixed-valence state as the molecular magnets, have shown that the Mn atom is in an intermediate valence state in the ferromagnetic phase. XMCD at the Mn K edge is then suitable for studying the electronic state of Mn atoms in the molecular magnets. Taking into account that the chemical shift between formal Mn^{3+} and Mn^{4+} at the Mn K edge is about 4 eV [4], we would expect to get two dichroic signal separated in energy if both the $3d^4$ and $3d^3$ electronic configurations were distinguished for the Mn atoms. We note here that XMCD experiments have already been performed at the Mn $L_{2,3}$ edges in the Mn_{12}Ac compound [5] but

the distinction of two oxidation states (+3 and +4) for Mn atoms was highly dependent on the applied theoretical model.

EXPERIMENTAL

The samples used in this study were crystallites of Mn_{12}Ac and Mn_4OAc . They were synthesized as described in Ref. 6. Powder samples of $\text{LaMn}_{0.5}\text{Ga}_{0.5}\text{O}_3$ (formal Mn^{3+}), $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ (formal Mn^{4+}) and $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (formal $\text{Mn}^{3.33+}$) have been used in order to obtain reference XMCD spectra. They were prepared following a conventional ceramic procedure [4,9,10]. All the samples were mounted uniformly on Scotch tapes for x-ray absorption measurements. Thickness was optimized to obtain the best signal-to-noise ratio.

Mn K-edge XMCD and XANES spectra were measured in transmission mode by the helicity-modulation (HM) method [7] on BL39XU at Spring-8. A 0.45 mm-thick diamond crystal slab was used in the Laue geometry with the 220 reflection plane in order to produce circularly polarized X-rays having plus and minus helicities in the a.c. mode with a frequency of 30 Hz by using a piezo oscillator. XMCD spectra were then obtained as the difference of the absorption coefficient $\mu_c = \mu^- - \mu^+$ for antiparallel μ^- and parallel μ^+ alignment of photon helicity and sample magnetization and they were normalized by the edge jump in XANES spectra. All the measurements were carried out at a fixed temperature of 5 K and with an applied magnetic field of 5 T where all samples are ferri- or ferromagnetic.

RESULTS AND DISCUSSION

Figure 1 shows the XMCD spectra at the Mn K-edge in $\text{LaMn}_{0.5}\text{Ga}_{0.5}\text{O}_3$ (Mn^{3+} reference) and $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ (Mn^{4+} reference) together with the XANES and its derivative spectra. For the XANES spectra, it is noted that the absorption edge energy in $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$, determined from the first inflection point, shifts by about 3 eV to a higher energy compared with that in $\text{LaMn}_{0.5}\text{Ga}_{0.5}\text{O}_3$. This energy shift correlates with the increasing formal valence state of Mn atoms from $\text{Mn}^{3.08}$ in the Ga compound up to $\text{Mn}^{3.8}$ in the Ni one.

The XMCD spectra show a similar profile for the two samples with the largest magnitude of the effect at the main absorption edge. The same chemical shift as for the XANES is also observed. The weak negative signal (B) at the rising edge indicates a small orbital magnetic polarization of the Mn 4p-band caused by interaction with the magnetic 3d shell [8].

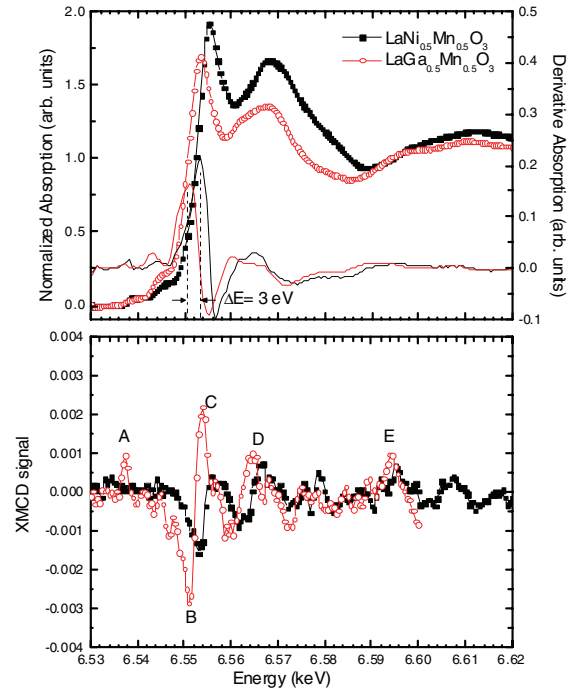


FIGURE 1. Mn K-edge in $\text{LaMn}_{0.5}\text{Ga}_{0.5}\text{O}_3$ and $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ at 5K, Top: XANES and its derivative spectra at and Bottom: XMCD spectra.

Their relative intensities are a factor of about 2, which is reasonable and consistent with bulk Mn magnetization properties of both samples. The magnetization achieves $4.05 \mu_B/\text{Mn}$ at 5T for $\text{LaMn}_{0.5}\text{Ga}_{0.5}\text{O}_3$ [9] whereas a magnetic moment of $1.8 \mu_B/\text{f.u.}$ is found for $\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ [10]. In addition, a pre-edge structure at 6537.5 eV (dipole forbidden $1s \rightarrow 3d$ transition, symmetry allowed due to the Mn 3d-O 2p mixing) and two positive peaks at ~ 14 and ~ 43 eV higher than the edge are observed, labeled as A, D and E, respectively. Peak D probably originates from magnetic multiple scattering of nearest-neighbor La and Mn atoms [11]. Peak E is associated with a multielectron excitation (MEE) as at this point, the energy is high enough to excite 1s and 3p electrons simultaneously.

Figures 2 and 3 show XANES and XMCD spectra at the Mn K-edge in the mixed valence manganite $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and the two molecular magnets Mn_{12}Ac and Mn_4OAc , respectively. The XMCD spectrum for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ is comparable to previously published data [4,12]. For $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, the dichroic signal at the Mn K-edge reveals the same derivative-like shape as for the Mn^{3+} and Mn^{4+} references. The peak B intensity at the absorption edge (E_0) is about -2.8×10^{-3} , similar in magnitude to that for $\text{LaGa}_{0.5}\text{Mn}_{0.5}\text{O}_3$.

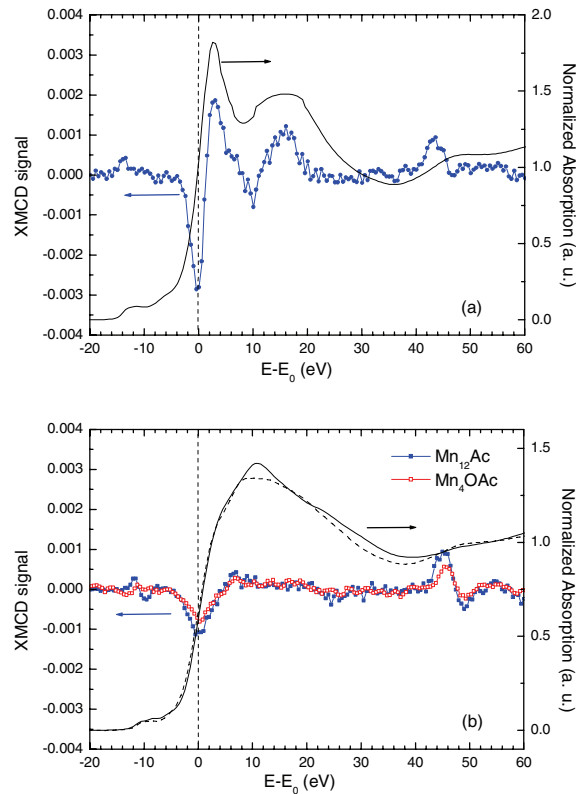


FIGURE 2. Mn K-edge XMCD spectra aligned at the absorption edge (left) and XANES spectra (right) at 5K. (a) in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ($E_0=6551.9$ eV) and (b) in Mn_{12}Ac and Mn_4OAc ($E_0=6548.8$ eV and 6548.4 eV, respectively).

This value is reasonably consistent with an average Mn valence of +3.36 and magnetic moment of $3.45\mu_B$ at the Mn site. Comparing to the molecular magnets, the peak B intensity gets smaller, over -1.1×10^{-3} and -8×10^{-4} for Mn_{12}Ac and Mn_4OAc , respectively; that is about a factor 2.5 and 3.5 smaller of that in the $x=0.33$ manganite. This reduction in the intensity can be associated with the ferrimagnetic structure of both molecular compounds. According to the results of polarized neutron diffraction in Mn_{12}Ac [3], magnetic moments of $3.69\mu_B$ and $3.79\mu_B$ were deduced for the two inequivalent Mn in the external ring and a value of $-2.34\mu_B$ was obtained for other Mn in the tetrahedral core, which gives an average magnetic moment of $1.7\mu_B/\text{Mn}$. Furthermore, the width of peak B is larger for the Mn clusters than for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. Hence, the present data suggest the contribution of two distinct dichroic signals in the case of the molecular magnets whereas a unique dichroic signal is deduced for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. In addition, the signal amplitude of peaks C and D at ~ 3 and ~ 14 eV above the edge decreases remarkably. This is also consistent with the

presence of distinct Mn atoms in symmetry-inequivalent sites, which can give rise to destructive interference effects in the magnetic multiple scattering.

CONCLUSION

We have measured XMCD spectra at the Mn K in different mixed-valence manganites and the Mn_{12}Ac and Mn_4OAc molecular magnets. Weak signals were observed around the absorption edge for all the samples, which reflect orbital magnetization of Mn p-band. By simple comparison of the XMCD spectra between bulk $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and the molecular magnets, with similar Mn formal mixed-valence state, a decrease in intensity and an increase in width of the negative peak at the absorption edge were observed for the molecular magnets. The reduction in intensity is consistent with their ferrimagnetic structure in contrast with the ferromagnetic one of bulk $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. On the other hand, the larger width suggests the presence of two dichroic signals correspondent to the presence of two electronic configurations for the Mn atoms in the molecular magnets.

ACKNOWLEDGMENTS

The authors thank Dr. G. Aromí and Dr. F. Luis for providing Mn_{12}Ac and Mn_4OAc samples, Dr. N. Kawamura of SPring-8 for technical support and Dr. J. Chaboy for his assistance and fruitful discussions. Supported by Spanish CICYT project N° MAT2005-04562 and from DGA and carried out under the approval of SPring-8 PRC (No. 2005A0178-NSc-np-Na).

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