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Journal of Electron Spectroscopy and Related Phenomena 86 (1997) 115–118

JOURNAL OF
ELECTRON SPECTROSCOPY
and Related Phenomena

Soft X-ray magnetic circular dichroism study of the colossal magnetoresistance compound $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

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Abstract

Soft X-ray magnetic circular dichroism (SXMCD) measurements are reported on the O K- and Mn L-absorption edges of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.15, 0.18, \text{ and } 0.4$) single crystals in their ferromagnetic regime. This has been done using a recently developed experimental technique for magnetizing the samples offering the possibility to get high-accuracy SXMCD effect measurements on bulk samples. The very strong doping-induced O K-edge intensity is proof of an enhanced O 2p hole component of the doped holes. O K soft X-ray magnetic circular dichroism spectra give evidence for an orbital magnetic moment of this O 2p component ferromagnetically coupled to the Mn moments. © 1997 Elsevier Science B.V.

Keywords: Soft X-ray magnetic circular dichroism; Ferromagnetic regime

After more than 40 years of rest the $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) perovskites are suddenly at the centre of attention again because of the discovery of the colossal magnetoresistance at temperatures close to room temperature [1].

The strong interplay between magnetism and electrical conductivity in these materials is conceptually understood in terms of the Zener double exchange (DE) model [2]. The extremely large change in the resistivity at the ferro- to paramagnetic transition as well as the huge discrepancy between the experimentally derived resistivity and its theoretical counterpart in the paramagnetic phase led Millis

et al. [3] recently to suggest a polaronic localization mechanism in addition to double exchange for the large resistivity changes.

Another very important aspect of these materials which is not sufficiently appreciated is the fact that such compounds involving high-oxidation state 3d transition metal (TM) ions should be expected to be charge transfer like compounds in which the holes introduced by doping are primarily on the O 2p orbitals rather than within the TM 3d orbitals as for example in cuprate high-temperature superconductors (HTSCs). The estimates of parameters [4] strongly suggest that LaMnO_3 should be classified as a charge transfer system within the scheme by Zaanen, Sawatzky, and Allen (ZSA) [5] much like the HTSCs.

In this contribution we present a soft X-ray magnetic circular dichroism (SXMCD) study of this compound from which we conclude that the doped

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holes have a strong O 2p component. The O orbital magnetic moment evidenced by our measurements is ferromagnetically coupled to the Mn moments.

The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ single crystals have been grown using the travelling solvent floating zone (TSFZ) method. Details on the crystal growth can be found elsewhere [6]. SXMCD experiments have been performed at the AT&T U4B Dragon beamline located at the National Synchrotron Light Source, Brookhaven National Laboratory. For the SXMCD measurements circular polarized light with a degree of polarization of 88% has been used. A magnetic field of ± 0.59 Tesla has been applied for magnetizing the samples using a Magnetic Mangle consisting of four transversally magnetized Nd–Fe–B permanent magnet rods with a remanence of 1.2 T. The helicity of the incoming light has been kept constant during the photon energy scans of the monochromator whereas the magnetization of the samples was flipped parallel/antiparallel to the propagation direction of the soft X-ray beam with a switching frequency of 0.2 Hz for each photon energy. This procedure has the advantage to avoid artifacts in the SXMCD difference spectra resulting from slightest energy shifts of the monochromator or from monitor current normalization problems resulting from stray light or higher order light.

In Fig. 1(a) we show O K-edge X-ray absorption spectroscopy (XAS) measurements for $x = 0.15, 0.18$ and 0.4 taken at 30 K with the field vector of the incoming linear polarized light being parallel to one of the crystallographic axes of the pseudocubic unit cell. These concentrations were chosen to represent materials below, slightly above, and well beyond the dopant concentration of the low-temperature metal–insulator transition. The part of the spectrum between 528 and 533 eV is in general interpreted as originating from unoccupied O 2p states in the ground state covalently mixed with Mn 3d states. In this interpretation the structures would represent the crystal field and Coulomb interaction multiplet structure of the Mn 3d electron addition states with e_g and t_{2g} symmetry. The total integrated intensity in this region is very large due to the large covalent mixing in the ground state as well as due to the charge transfer insulator character of the undoped LaMnO_3 . Thus, the doped holes have a considerable O 2p character even larger than has been the case for the HTSCs.

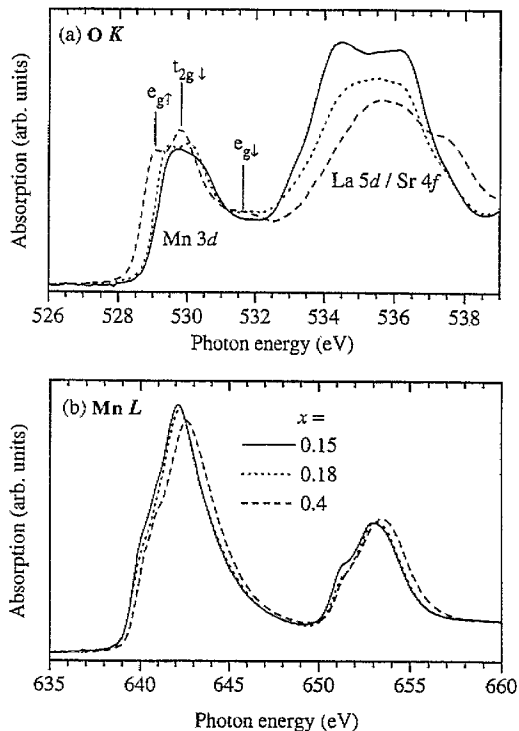


Fig. 1. (a) O K and (b) Mn L XAS spectra of single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The spectra are normalized between 585 and 595 eV and between 684 and 694 eV in the case of the O K and Mn L absorption edges, respectively.

The three peaks at 529.1, 529.8 and 531.6 eV for $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ have in the past been interpreted as being due to transitions into $e_{g\uparrow}$, $t_{2g\downarrow}$ and $e_{g\downarrow}$ states (\uparrow and \downarrow describing majority and minority spin), respectively, resulting in a peak assignment as given in Fig. 1(a). The actual assignment of these pre-edges is still a matter of controversy [4,7]. For the actual purpose, however, it is important to note that the pre-peak at 529.1 eV has in all cases been interpreted as being of Mn 3d $e_{g\uparrow}$ majority character depleted by doping.

In Fig. 1(b) the Mn L XAS spectra are shown with the field vector of the incoming linear polarized light being parallel to one of the crystallographic axes of the pseudocubic unit cell. According to dipole selection rules excitations into unoccupied states with mainly Mn 3d character are realized. When going from lower to higher Sr concentrations a shift to higher photon energies of both the L_{III} and L_{II} absorption edges can be observed. This so-called

chemical shift is due to higher Mn 2p core level binding energies resulting from a decrease in the Mn 3d electron count with increasing x . Furthermore, there is a distinct decrease in the L_{III} to L_{II} branching ratio which also indicates a reduction of the 3d electron count as could be established for the high-spin ground state of transition metal compounds. From these findings together with the changes in the O K absorption edges it can be concluded that the doped charge carriers in $La_{1-x}Sr_xMnO_3$ have a strongly mixed Mn 3d–O 2p character.

We now discuss the magnetic properties of these systems. In Fig. 2 we present the O K SXMCD spectra of $La_{0.82}Sr_{0.18}MnO_3$ and $La_{0.6}Sr_{0.4}MnO_3$ taken at 30 K well below their ferromagnetic Curie temperature, together with the corresponding difference spectra. From this, it can be seen that there is a SXMCD effect

of about 3% in the first low-energy prepeak which has been assigned to O 2p orbitals hybridized Mn 3d states with $e_g \uparrow$ majority character. From the fact that the sign of the SXMCD effect in the O K edges is the same as that of the Mn L_{III} edges (see Fig. 3(a)) it can be concluded that there is a ferromagnetic coupling between the magnetic moment on the O sites and the Mn moments. The amplitude of the SXMCD effect stays the same when going from $x = 0.18$ to $x = 0.4$, indicating that the orbital magnetic moment on the O ligands does not change significantly with doping.

Fig. 3(a) shows the Mn L SXMCD spectrum of $La_{0.6}Sr_{0.4}MnO_3$ taken at 30 K together with the corresponding difference spectrum and the integrated difference spectrum in Fig. 3(b). A large SXMCD effect of 24.9% is observed at the minimum of the strong negative peak in the SXMCD difference

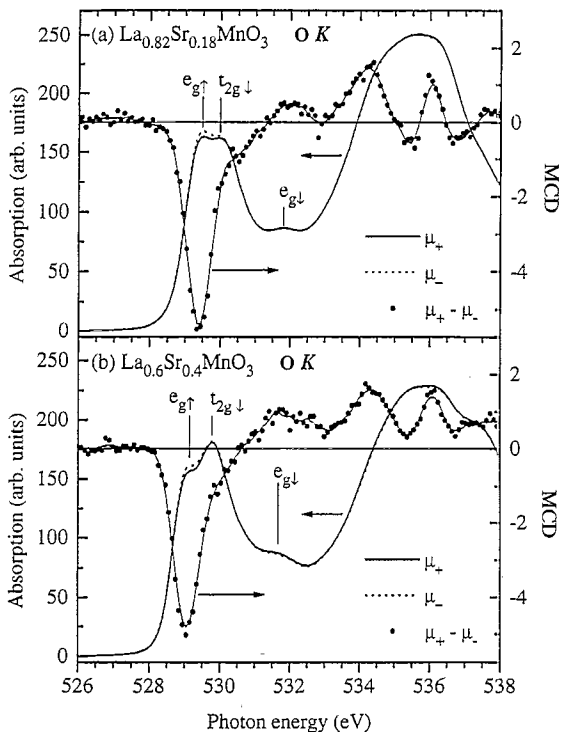


Fig. 2. O K soft X-ray magnetic circular dichroism spectra of (a) $La_{0.82}Sr_{0.18}MnO_3$ and (b) $La_{0.6}Sr_{0.4}MnO_3$; solid (dotted) lines: spectra taken with the spin of the incident photons parallel (antiparallel) to the spin of the Mn 3d majority electrons. Solid circles: SXMCD difference spectra resulting from the above data after correction for the finite degree of circular polarization of 88%. The thin solid lines are guides to the eye.

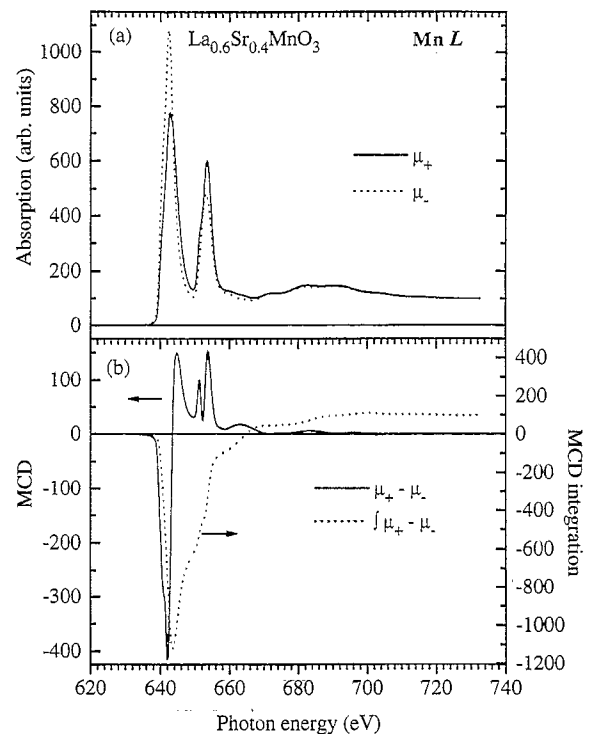


Fig. 3. (a) Mn L SXMCD spectra of $La_{0.6}Sr_{0.4}MnO_3$; solid (dotted) line: spectra taken with the spin of the incident photons parallel (antiparallel) to the spin of the Mn 3d majority electrons. (b) Solid line: SXMCD difference spectrum resulting from the above data after correction for the finite degree of circular polarization of 88%; dotted line: integrated difference spectrum.

spectrum within the energy range of the Mn L_{III} edge. The Mn orbital moment was derived from these data using SXMCD sum rules [8]. We get a large Mn orbital magnetic moment for the $x = 0.4$ compound of $0.055 \pm 0.013 \mu_B$ assuming a Mn 3d electron count of 4.04 in accordance with the amount of ligand hole character within the Mn³⁺ and Mn⁴⁺ ground states [4].

In summary, we have reported on SXMCD experiments on the O K- and Mn L-edges of La_{1-x}Sr_xMnO₃ in the conducting ferromagnetic phase using a new experimental technique for magnetizing the samples. A net orbital magnetic moment within the O 2p shell has been evidenced from the SXMCD O K-edges ferromagnetically coupled to the neighbouring Mn moments. Standard XAS data give support for the heavily mixed O 2p/Mn 3d character of the doped holes.

Acknowledgements

EP acknowledges financial support by the European Union under Contract No. SC1 CT91-0751. This investigation was supported by the Netherlands Foundation for Chemical Research (SON), the Netherlands Foundation for Fundamental

Research on Matter (FOM) with financial support from the Netherlands Organization for the Advancement of Pure Research (NWO). The experimental part of this work has been performed at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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