Evidence for Mn^{2+} ions at surfaces of $La_{0.7}Sr_{0.3}MnO_3$ thin films

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We present a detailed investigation of the valence of manganese sites at the surface of colossal magnetoresistance $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films by x-ray absorption spectroscopy (XAS). The XAS Mn L-edge spectra of epitaxial LSMO films usually show a peak or shoulder at 640 eV. Differences in the intensity of this feature are commonly attributed to slight changes in the Mn^{3+}/Mn^{4+} ratio or the crystal field strength. By comparison of different XAS spectra of LSMO thin films with the known multiplet structure of Mn^{2+} in a cubic crystal field, we assign this 640-eV feature to Mn^{2+} ions. XAS with increased surface sensitivity, combined with photon energy-dependent photoelectron spectroscopy measurements of the Mn(3s) exchange splitting, show that the Mn^{2+} species are mainly located at the surface. The Mn^{2+} scenario indicates significant modification of the LSMO surface with respect to the bulk properties that should be taken into account in all the charge and spin tunneling and injection experiments.

I. INTRODUCTION

Rare-earth manganese perovskites have attracted considerable attention due to their unusual electronic structure and the strong interplay between magnetic ordering and charge transport properties. They exhibit a wide range of magnetic and structural transitions, and feature a colossal negative magnetoresistance.[1] The electrical and magnetic properties of the manganites are mainly determined by the Mn valence, which is traditionally described as a mixture of Mn^{3+} and Mn^{4+}, correlated with the ratio between trivalent and divalent cations as well as the oxygen (non)stoichiometry.[2]

It has been shown that $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) is a half-metallic[3] material being characterized by full spin polarization of charge carriers well below the Curie temperature. The half metals are very attractive for spintronics applications as they allow one to overcome the conductivity mismatch limitation for the direct spin-polarized injection at the ferromagnetic-semiconductor interface.[4] Spin-injection and spin-polarized tunneling in a number of prototypical devices based on LSMO and other manganese perovskites has been reported.[5–7] Moreover, LSMO was recently found to provide significant spin-polarized injection at hybrid inorganic/organic interfaces.[8,9]

Considering spin injection, the *surface* magnetic and electronic properties are of paramount importance. It is well known that the surface composition of thin films of rare-earth manganese perovskites differs from the bulk, due to segregation effects.[10,11] In LSMO, Sr segregation may even lead to the formation of $SrO/SrCO_3$ species at the surface.[12,13] In addition, the oxygen content, especially near the surface, depends critically on the thermal history. So far, Sr segregation and variations in oxygen content were known to influence the surface Mn valence by shifting the balance between Mn^{3+} and Mn^{4+}. However, we show in this paper that the behavior at the surface is more complex. We demonstrate by x-ray absorption spectroscopy (XAS) and photo-electron spectroscopy (PES) the presence of Mn^{2+} ions at LSMO surfaces. The abundance of these Mn^{2+} ions should strongly influence the surface magnetic and electrical properties.

To date, a large number of XAS studies of LSMO have been reported that describe its electronic structure in an element-specific fashion. The Mn L-edge spectra can be interpreted using atomic multiplet theory.[14] To simulate experimental spectra of LSMO, calculations for Mn^{3+} and Mn^{4+} ions are summed up with appropriate weights. It has recently been shown that even though the Mn 3d states are hybridized with 2p oxygen orbitals, a reasonable quantitative description is provided by atomiclike theory taking into account the presence of 2p core holes.[15] Although the Mn L-edge spectra are quite well understood, there are considerable differences in the spectra of $La_{0.7}Sr_{0.3}MnO_3$ in the literature, which remain so far largely unexplained. In a number of cases, a pronounced structure at 640 eV photon energy (i.e., close to the onset of the x-ray absorption edge) is observed,[15–17] while in other cases this structure appears at most as a very weak shoulder on the main peak.[18] From experimental XAS data of a range of $La_{1-x}Sr_xMnO_3$ samples with different x, it has been concluded that the 640-eV peak is related to the presence of Mn^{4+} ions.[17] Theoretical calculations show that the intensity of this peak not only depends strongly on the Mn^{3+}/Mn^{4+} ratio, but also on the crystal field strength.[14] Based on this argument, differences between the spectra of $La_{0.7}Sr_{0.3}MnO_3$ with different capping layers were explained by small changes of these two parameters due to a variation in defect concentrations such as oxygen vacancies.[15] In this paper, we present a different interpretation, based on experimental evidence showing that the 640-eV feature is related to Mn^{2+} ions, which are present at the surface. Our results therefore contribute to settling a long-standing debate about the details of XAS spectra of LSMO.

II. EXPERIMENT

LSMO films were deposited on matching NdGaO$_3$ (NGO) and SrTiO$_3$ (STO) substrates as well as nonmatching Si substrates using the Channel-Spark deposition method.[19] During deposition substrates were heated to 800–850 °C in the case of STO and NGO substrates and to 650–700 °C for Si, while the oxygen pressure was kept at 10^{-2} mbar. The films were annealed at 400–450 °C in high vacuum after deposition in order to remove overoxygenation effects. Epitaxial LSMO films exhibit a high Curie temperature ($T_C \sim$ 350–370 K) and a resistivity lower than 10 mΩ cm at 300 K. Micro-Raman analysis of these films showed that they are essentially rhombohedral, with the structural phase showing a ferromagnetic metallic state. Some orthorhombic inclusions are present, of which the structural phase is characterized by a strong Jahn-Teller distortion, corresponding to an insulating paramagnetic phase. The nonepitaxial, polycrystalline LSMO films on Si are also ferromagnetic at room temperature.

XAS, PES, and x-ray magnetic circular dichroism (XMCD) measurements were performed at beamline D1011 of the MAX-II storage ring, located at the MAX-Laboratory for Synchrotron Radiation Research in Lund, Sweden. The end station is equipped with a Scienta ESCA200 hemispherical electron analyzer for PES and a purpose build multichannel plate (MCP) detector for XAS. The MCP detector setup contains an electron suppression grid, enabling both total and partial electron yield measurements. The depth sensitivity of the XAS measurements could be varied by changing the suppression voltage. For both the XAS and XMCD measurements, the angle of incidence of the photon beam was set to 60° relative to the sample normal. For XMCD, the in-plane magnetization of the LSMO films was set by applying a magnetic field pulse of about 200 G. The XMCD spectra were recorded with a fixed helicity of the light and opposite magnetization directions.

The photon energy resolution was kept below 100 meV. The photon energies were calibrated using Au(4f) PES spectra, recorded with both first- and second-order output light of the beamline D1011 monochromator. The combined first- and second-order measurements allow for a distinction between the monochromator (photon energy) and electron-analyzer (electron kinetic energy) offsets.

The effects of annealing in vacuum (10^{-6} mbar) or in an oxygen atmosphere were studied by XAS measurements, performed at the end station of the SB7 beamline of the Super ACO storage ring at LURE (Orsay, France). Samples were annealed at 450 °C by using a filament placed near the backside of the substrate. The oxygen atmosphere was supplied by placing a nozzle in front of the heated surface, through which oxygen gas was leaked in such that the pressure in the chamber was 10^{-4} mbar. After every annealing procedure, the surface purity was checked by x-ray photoelectron spectroscopy.

III. RESULTS AND DISCUSSION

Figure 1 shows Mn L-edge XAS spectra of two different epitaxial LSMO thin films, a XAS spectrum of MnO taken
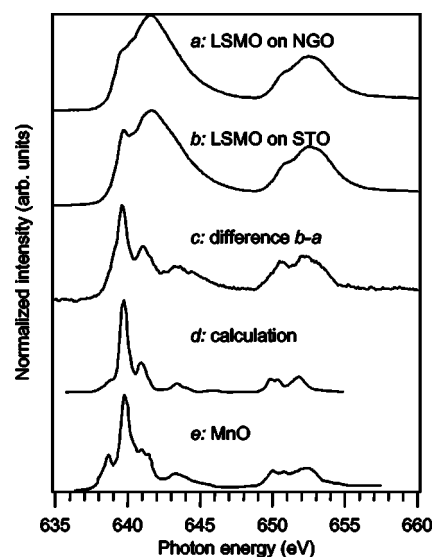

FIG. 1. Total-electron-yield XAS spectra of two different epitaxial LSMO films, on NGO (a) and STO (b), difference curve (c) obtained by subtracting the weighted XAS spectrum a from b, calculated XAS spectrum (d) of Mn^{2+} in a cubic crystal field with Dq=0.6 eV taken from Ref. 9, and XAS spectrum of MnO (e) taken from Ref. 14.

from Ref. 20 and an atomic multiplet calculation of a Mn^{2+} ion in a cubic crystal field taken from Ref. 14. The intensity of the shoulder and peak at 640 eV photon energy is clearly different for the two LSMO samples (curves a and b). This feature depends on a variety of factors characterizing sample quality and especially on post-deposition thermal history as will be shown below. The differences between XAS spectra a an b become much clearer upon subtraction of a, with the appropriate weight, from b. Weighting of a to a value up to 87% of the spectral weight of b provided reasonable difference spectra. The difference spectrum c shown in Fig. 1 was obtained by setting the area of a to 82% of that of b. The resulting curve (c) is very similar to the Mn L-edge spectrum of MnO [e (Ref. 20)] and the atomic multiplet calculation for Mn^{2+} with a cubic crystal field splitting of 0.6 eV.[14] This strongly suggests that the differences between a and b are due to the presence of Mn^{2+} ions in different abundance rather than variations in the Mn^{3+}/Mn^{4+} ratio or crystal field strength.

As for the Mn^{4+}/Mn^{3+} ratio, it is reasonable to expect that the Mn^{2+} content can be changed drastically by oxygenation procedures. Figure 2 shows XAS spectra of the same epitaxial LSMO thin film, as prepared (I), after annealing at 450 °C (II) in UHV, and in 10^{-4} mbar of oxygen (III). Upon annealing in vacuum, which is known to remove oxygen from LSMO,[7] the XAS spectrum is dominated by the sharp features that we assign to Mn^{2+} ions. These features are strongly suppressed after subsequent annealing in an oxygen atmosphere, in qualitative agreement with the Mn^{2+} scenario.

In order to distinguish between bulk and surface Mn^{2+} contributions, we performed PES and XAS experiments with different surface sensitivity on a sample that showed a pronounced sharp XAS peak at 640 eV, a polycrystalline LSMO film on Si. Besides the fingerprint for Mn^{2+} in XAS (see
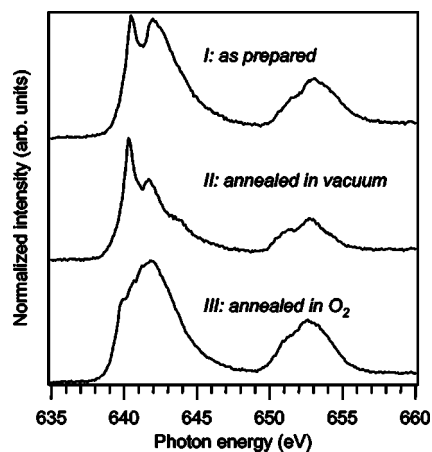
FIG. 2. XAS spectra of an epitaxial LSMO film on STO, as prepared (I), after annealing at 450 °C in vacuum (II), and after annealing in O_2 (III, O_2 pressure in chamber 10^{-4} mbar).

FIG. 3. XAS and XMCD curves of LSMO on Si at $T=130$ K, a surface-sensitive XAS spectrum of the same sample recorded with a 500 V e^- suppression voltage (top), and Mn(3s) PES spectra (inset) measured with hv$=220$ eV (A) and hv$=1000$ eV (B).

Fig. 1), we employ PES measurements of the Mn(3s) exchange splitting to discriminate between Mn with different valence.[21] The probing depth was reduced by decreasing the photon energy for PES and by applying a 500-V suppression voltage on the MCP detector in XAS measurements. This voltage eliminates the majority of secondary electrons and decreases the probing depth from about 50–100 Å to roughly 10 Å.[22] We used 1000 and 220-eV photons for the Mn(3s) PES measurements. For these photon energies, the elastic mean free path λ for Mn(3s) photoelectrons changes from $\sim$18 to $\sim$5 Å, as calculated with the semiempirical model developed by Tanuma et al.[23]

Figure 3 shows XAS, XMCD, and Mn(3s) PES spectra of LSMO on Si. The XAS spectra recorded without suppression voltage (bottom curves)—i.e., in total-electron-yield mode—show a rather strong peak at 640 eV, but are otherwise similar to the previously shown XAS spectra of epitaxial LSMO films. Upon applying a 500-V suppression voltage (top curve), the sharp structure in the XAS spectrum associated with Mn^{2+} is strongly enhanced, indicating that the Mn^{2+} ions are located near the surface. The Mn(3s) PES spectra (inset) confirm this. For $hv=1000$ eV ($\lambda=18$ Å, spectrum B) the exchange splitting is estimated as 5.5 eV, corresponding to an average Mn valence close to Mn^{3+} (Ref. 21). The exchange splitting increases to 6.6 eV for $hv=220$ eV ($\lambda=5$ Å, spectrum A)— i.e., even larger than the experimentally observed value of 6.2 eV for divalent Mn in MnO (Ref. 21) and similar to 6.5 eV for Mn^{2+} in MnF$_2$ (Ref. 24).

Figure 3 also shows the XMCD curve, obtained by taking the difference between XAS spectra with in-plane magnetization parallel (M_p) and anti-parallel (M_a) to the helicity of the circularly polarized light. The sample was kept at $T=130$ K during these measurements, while the angle of incidence of the photon beam was 60° relative to the sample normal. Even though LSMO on Si is polycrystalline, it is clearly ferromagnetic with an XMCD curve similar to those of epitaxial LSMO films.[16,18] It is interesting to note that the peak at 640 eV photon energy does not display any significant XMCD effect, whereas the XAS intensities for the other
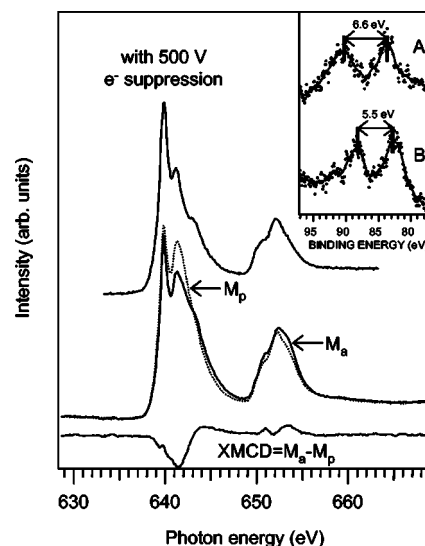
spectral features depend strongly on the magnetization direction.

At this moment we cannot identify in a straightforward way the nature of the Mn^{2+} ions: both a static and a dynamic situation can be considered. In a static picture, one would expect the formation of MnO inclusions. Although the MnO inclusions cannot be ruled out completely and could in principle explain the insulating defects observed on the surface of LSMO thin films,[25] this scenario is in some contradiction with oxygen annealing effects. Indeed, it is difficult to expect any reversible conversion of Mn from MnO sites into manganite ones. A possible reason for the dynamic Mn^{2+} presence can be the valence instability of the Mn^{3+} ions to the creation of Mn^{4+} and Mn^{2+} species. Such an instability would not necessarily modify the "bulk" magnetic and electrical properties of the manganite, and can be driven by the surface as an extended defect.

Dynamical inhomogeneities as well as phase separation are commonly observed in manganites[26] and are crucial for their properties. The presence of Mn^{2+} ions can be interpreted in this framework even though further investigations are required to support this picture.

IV. CONCLUSIONS

By comparing differences in XAS absorption spectra of epitaxial LSMO thin films with published XAS spectra of MnO and atomic multiplet calculations of Mn^{2+} XAS, we assign the peak or shoulder at 640 eV in the XAS spectrum of LSMO to Mn^{2+} ions. XAS experiments with increased surface sensitivity show that the Mn^{2+} species are localized at the surface. This is confirmed by photon-energy-dependent PES measurements of the Mn(3s) exchange splitting. Annealing in UHV results in a strong increase of the peak assigned to Mn^{2+}. By subsequent in situ exposure to oxygen,

the Mn^{2+} fingerprint is strongly reduced from the XAS spectra, as a consequence of the increased value of the manganese valence state.

It can thus be concluded that a simple description of the Mn valence in terms of a mixed Mn^{3+}/Mn^{4+} state is not valid at the surface. Depending on the exact nature of the additional Mn^{2+} species, the surface electronic structure might be altered by an increase in the occupation of Mn(3d)-derived e_g states. Since the XAS signals associated with Mn^{2+} do not show any significant XMCD effect, the magnetic properties of the LSMO surface and its spin polarization are expected to be strongly modified by the presence of Mn^{2+} ions. Our results contribute to shed light on the peculiar electronic surface states in LSMO compounds and clarify the nature of

spectroscopic signatures in their XAS spectra that are routinely used to study their electronic and magnetic properties.

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