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Local anisotropy in strained manganite thin films

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We report on an angular resolved x-ray absorption spectroscopy study of the local atomic structure around the manganese ions in $La_{0.7}Sr_{0.3}MnO_3$ thin films epitaxially grown on tensile and compressive substrates. *Ab initio* calculations provide strong support to the analysis of the experimental data and make possible the unambiguous derivation of a model of local distortion around the manganese atoms, without modification of the tilt angle Mn–O–Mn, among the octahedra. This distortion, tending to localize the charge carriers, is the driving parameter in the modifications of the magnetic and transport properties observed in thin films with respect to bulk systems. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1623936]

The spectacular versatility of magnetic and transport properties observed in mixed manganites, and the dependence of these properties on structural parameters have open up many expectations for the design of tunable magnetic devices.[1,2] This versatility turns also the manganite alloys very rich model system for fundamental studies, like spin-transport in half metallic ferromagnets, i.e., ferromagnetic metals with 100% spin-polarized conduction band. For bulk rare-earth manganese oxides, the local structure such as Mn–O–Mn angle and Mn–O bond length can be varied by changing the doping concentration or by applying hydrostatic pressure. In thin films, the substrate-induced crystallographic distortions are anisotropic, unlike the distortions obtained by hydrostatic pressure or cation substitution. Structural and magnetic studies of thin films on slightly mismatched substrates have shown the significant sensitivity of manganite properties to the substrate induced structural modifications, as the decrease of the Curie temperature with the increase of the external strains.[3–5] Due to the double exchange mechanism, which induces ferromagnetism and metallicity, the Mn–O distances (coordination length) and the Mn–O–Mn angle (octahedral tilt) are the relevant local scale parameters determining the magnetism and transport properties in manganites films. It is then specially important to explicit the connection between the crystallographic cell strains and the modifications that they induced in these parameters.[1,2,6] Some experimental studies using x-ray absorption spectroscopy have already been performed to address the local order in manganites films.[3,7] However, at the present day, no consensus has been reached about the origin of the main effect, alteration of the coordination length,[3,8] or of the octahedral tilt.[7]

In this letter, we report on an angle resolved x-ray ab-sorption spectroscopy study, combining experimental measurements and *ab initio* calculations, in $La_{0.7}Sr_{0.3}Mn_3$ (LSMO) thin films epitaxially grown on tensile and compressive substrates. The modifications in the x-ray absorption near edge structure (XANES) spectra are correlated to modification in the average Mn–O bond distance and distortion of the MnO_6 octahedra and we show that the strain-induced local modifications around the manganese atoms are fully accommodated in the coordination shell, without change in the tilt angle Mn–O–Mn, among the octahedra.

LSMO manganites crystallize in a pseudocubic perovskite structure ($a = 3.87$ Å). They have a fully spin-polarized conduction band and exhibit ferromagnetic transition around room temperature. The LSMO thin films have been epitaxially grown by pulsed laser deposition under tensile {$SrTiO_3$ (STO) [001]} and compressive {$LaAlO_3$ (LAO) [001]} substrates with cubic ($a = 3.905$ Å) and pseudocubic ($a = 3.793$ Å) structures, respectively. The small lattice mismatch between LSMO, STO, and LAO allows a pseudomorphic growth for film thickness below 100 and 50 nm, respectively.[9] MgO substrate (cubic, with $a = 4.21$ Å) with large lattice mismatch (9%) was used to obtain an unstrained, fully textured films. For similar thickness the strain factor[6,9] ($\epsilon_{zz} - \epsilon_{xx}$, see Table I) is about twice for the film grown on

TABLE I. Films strain components ε_{xx} and ε_{zz} defined as $\epsilon_{xx} = \epsilon_{yy} = (a_{film} - a_{ref})/a_{ref}$ and $\epsilon_{zz} = (c_{film} - c_{ref})/c_{ref}$.

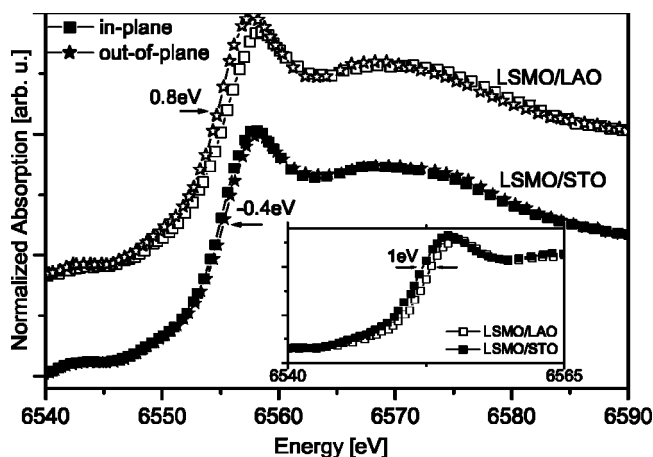| Substrate	Film thickness (nm)	$\epsilon_{xx} = \epsilon_{yy}$ (%)	ϵ_{zz} (%)
$SrTiO_3$ (tensile)	60	0.9	−0.8
MgO	60	0	0
$LaAlO_3$ (compressive)	45	−2.0	2.3

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FIG. 1. Near edge x-ray absorption spectra at the Mn K edge for the tensile ($SrTiO_3$) and compressive ($LaAlO_3$) LSMO film in plane and out of plane measurements. The energy shifts are in opposite directions and scaled in amplitude by a factor of 2. Inset compares the in plane measurements for both films.

FIG. 2. XANES *ab initio* calculations of the LSMO structure in the compressive and tensile films, considering orthorhombic distortion of the MnO_6 octahedron. The main plot shows comparison between the in-plane and out-of-plane orientations for each film. Inset: in plane calculations for both films.

LAO than for the film grown on the STO substrate. Further description of the growth conditions and structural characterization by the x-ray diffraction can be found elsewhere, together with a characterization of their transport and magnetization properties.[9]

The x-ray absorption experiments at the Mn K edge (6539 eV) were performed at the D04B-XAS beamline of the Brazilian synchrotron light laboratory [Laboratório Nacional de Luz Síncrotron (LNLS)] in Campinas, Brazil.[10] The monochromator was a Si (111) channel-cut crystal, an ion chamber monitored the incident beam and the data were collected in the fluorescence mode using a Ge 15-elements solid state detector. Selective information in the plane and out of the plane of the same film are obtained by setting the angle between electric field vector of the incident photon beam and the film surface to values close to 0° and 90° (10° and 75°, respectively). XANES spectra were collected in the range 6440 to 6700 eV with energy steps of 0.3 eV. The energy calibration of the edge was carefully checked by monitoring the slow energy shift of a Mn metal foil reference and the XANES were normalized at about 150 eV above the edge. The edge structure in all experimental spectra can be compared in position and intensity and energy shifts as small as 0.1 eV are certified.

Figure 1 shows the XANES spectra of the tensile (STO substrate) and compressive (LAO substrate) strained films. The energy shift at the edge between the spectra collected in the plane and out of the film plane can be associated to local changes on the average Mn–O bond distance. The interpretation of the pre-edge structure in the XANES spectra could provide relevant information on the local electronic structure around Mn atoms,[11] but it would require specific high resolution measurements and has not been included in this study. Taking the out-of-plane spectra as reference, the negative energy shift (-0.4 eV) in the in-plane spectrum for LSMO/STO is correlated to a larger average Mn–O bond length compared to the average out-of-plane bond length. In the film under compressive strain, the positive energy shift ($+0.8$ eV) indicates a smaller in-plane average Mn–O bond length as compared to the out-of-plane one. Comparison be-
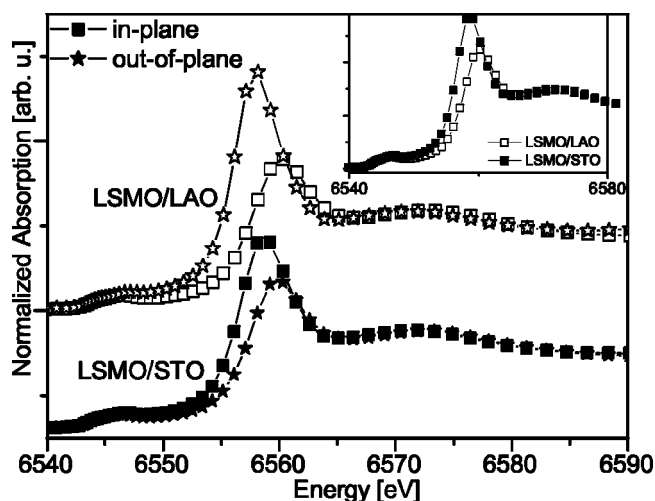
tween both films for the in-plane situation reveals a shift of 1 eV, attesting for an larger average Mn–O bond length for the film grown on the tensile substrate than for the film grown on the compressive one.

As expected, the shifts for the tensile and compressive films are in opposite directions. Moreover the amplitude of the shift for the LSMO/LAO film is about twice that for the LSMO/STO one, and of the same order as the ratio of the long range strain factor among these films (on Table I). The strain on the cell parameters is then directly related to average octahedral modifications. This indicates that the strain should be fully accommodated by changes in the coordination shell (Mn–O), without any modification of the Mn–O–Mn angle. This agrees with our previously reported extended x-ray absorption fine structure (EXAFS) results.[8]

Slight modifications of the line shape and intensity are also observed in the XANES spectra. Such modifications have already been reported by some authors,[3,12] and have been associated to distortions of the local structure. We performed *ab initio* simulation to address more precisely the actual consequence of the distortion of the octahedron on the XANES spectra and specially to investigate how far local distortion may account for the difference observed in the XANES spectra.

Self-consistent calculations were performed in the full multiple scattering approach using the FEFF8.2 code[13] that provides an accurate calculation of the Fermi energy. The real part of potential is modeled by an exchange-correlation Hedin–Lundqvist potential. All calculated absorption spectra were normalized by the value at 50 eV above the absorption edge allowing the *ab initio* calculations to be compared in position and intensity. Simulations were performed in a LSMO cluster considering isotropic MnO_6 and anisotropic octahedral distortions. As expected for the isotropic case, the spectra do not show any modification in position and shape of the edge main line among in-plane and out-of-plane situations. The calculations shown in Fig. 2 were performed for clusters with tetragonal distortion using local order parameters scaling with the crystallographic cell parameters of the

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films. We should point out that the calculations do not take into account structural disorder or dispersion of the Mn–O length, so that in the calculated XANES spectra the difference in amplitude are higher and the rising slope steeper than for the experimental data. With this restriction, the calculated structures reproduce well the main features of the experimental results. They account as well for the energy shift, in amplitude and direction, as for the relative reduction of the amplitude of the main feature close to the edge, among the two orientations for each film (Figs. 1 and 2). The differences for the in-plane case, among the two films are also nicely reproduced (Figs. 1 and 2, insets). Based on these calculations we can then certify a model of anisotropic distortion of the MnO_6 octahedron that accounts for the experimental XANES spectra.

In the LSMO system, the contribution of the spontaneous energy-lowering Jahn–Teller distortion of the $Mn^{3+}O_6$[4,14] is too small to be associated to a measurable average octahedral distortion. On the other hand, the substrate strain induces a larger and measurable static anisotropic distortion of the MnO_6 octahedron, with splitting of the in-plane and out-of-plane Mn–O bond lengths. This distortion leads to an increase of the splitting of the e_g levels tending to localize the charge carriers and explains the decrease of the temperature of ferromagnetic transition observed in thin films with respect to bulk systems.[9,15]

We must emphasize that the XANES modifications are due to changes on the local density of unoccupied states and are mainly correlated with modifications on the angles between the oxygens of the coordination shell, due to the splitting of the Mn–O bond length. This splitting may results from diverse kind of distortions of the MnO_6 octahedron. In a tetragonal local distortion of the MnO_6 octahedron, different Mn–O distances are found in-plane and out-of-plane, but only one distance exists in the plane. In an orthorhombic distortion, the in-plane and out-of-plane Mn–O distances are different, but with also different Mn–O distances for bonds in the plane. This later nonisotropic distortion in the plane may take place due to the nature of the Mn^{3+} and Mn^{4+} ions. Unfortunately, the change in the density of unoccupied states between these two situations is small and *ab initio* calculations yield almost the same results for tetragonal and orthorhombic distortions.

We performed careful measurements for the in-plane case by rotating the sample perpendicular to the beam propagation axis. For each individual sample all spectra were identical. We observed that the slope of absorption edge for strained and relaxed films are significantly different (Fig. 3). The absorption edge is broader in the case of the constrained films as compared to the relaxed one. This feature points to an increase of the disorder in the Mn–O bond lengths in the plane. In view of our previous EXAFS results,[8] this corroborate the hypothesis of an additional splitting for in-plane Mn–O bond lengths of strained films with respect to the relaxed case. A model of orthorhombic distortion should then better account for all experimental results than a model assuming only tetragonal distortion.

In summary, we presented here a combination of experimental measurements and *ab initio* calculations of polarized
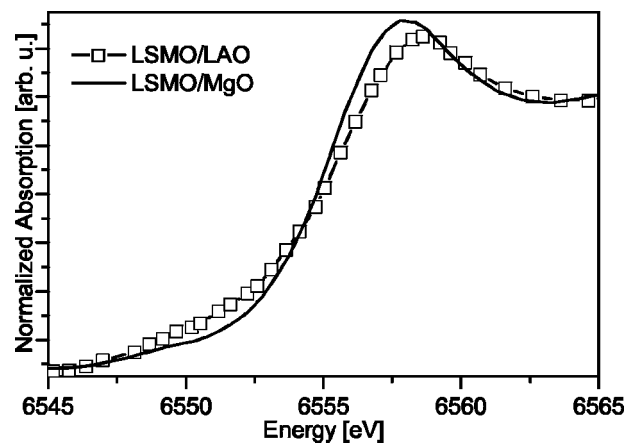

FIG. 3. Comparison between the relaxed and compressive film in the plane of the film. The decrease in the edge slope for the compressive film indicates an increase of the average distortion of the octahedra.

x-ray absorption to investigate the local scale structural distortion induced by substrate epitaxial strain around manganese atoms in $La_{0.7}Sr_{0.3}MnO_3$ films. We show that biaxial strain is locally accommodated in the coordination shell, by distortion of the MnO_6 octahedron, without change in the tilt angle. This distortion leads to an increase of the splitting of the e_g levels accounting for the decrease of the Curie temperature by increasing the external biaxial strain. Our results are compatible with an additional distortion in the plane of strained films, leading to an orthorhombic local symmetry.

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