Experimental and *ab initio* investigations of the x-ray absorption near edge structure of orthorhombic LuMnO₃

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(Received 5 April 2012; accepted 25 May 2012; published online 18 June 2012)

X-ray near edge absorption spectroscopy was used to probe the electronic structure of multiferroic orthorhombic LuMnO₃ polycrystalline samples and strained, twin-free orthorhombic (1–10) LuMnO₃ films grown by pulsed laser deposition on (1–10) YAlO₃ substrates. For all o-LuMnO₃ samples x-ray near edge absorption spectroscopy spectra reveal that the pre-edge structure is influenced by the increase in MnO₆ distortion as a result of the smaller *Re*-ion or film strain. Furthermore there is clear evidence of anisotropic Mn-O bonding and Mn orbital ordering along the *c*- and [110] direction. The experimental film and bulk data are in agreement with *ab initio* simulations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4729002>]

Today's information technology relies on the controlled manipulation of magnetic and dielectric respective ferroelectric properties of materials. To gain a further degree of freedom in material manipulation, a direct coupling between ferroelectricity (polarization) and magnetism (magnetic moment) is very attractive, because it would enable an electric control of magnetism and, by applying a magnetic field, a control over the electric polarization. The direct coupling between (anti)ferromagnetism and ferroelectricity, described as multiferroicity¹ as realized in the strongly correlated manganates, has attracted renewed interest.^{2–4} Extraordinary strong couplings have been discovered in material systems such as *Re*MnO₃ (Ref. 5) and *Re*Mn₂O₅ (Ref. 6) (*Re* = Y or other rare earth) where ferroelectricity arises directly from magnetic order as a result of a structural phase transition. Because of the magnetic origin of the electric polarization, these so-called magnetically induced ferroelectrics provide the most direct coupling between magnetic order and ferroelectricity. From a fundamental point of view the coupled order parameters will result in competing interactions, which are known to be beneficial for the emergence of phenomena and behaviour not known to exist in this combination. In addition, the proximity of such materials to quantum critical points makes them highly susceptible to small perturbations, a fact which can be used for a controlled manipulation of materials properties. Looking from an applications point of view, materials with directly coupled magnetic and ferroelectric properties are important for the development of devices with added functionalities, e.g., control of the electric charge via an applied magnetic field and spins by an applied voltage.

One of the best studied magnetically induced ferroelectrics is TbMnO₃, where magnetic order is established below *T* = 42 K, followed by a ferroelectric transition below

T = 27 K (Ref. 5), and the magnetic structure inversion symmetry is broken in the ferroelectric, but not in the paraelectric phase.⁷ The symmetry analysis of the magnetic structure using a magneto-electric coupling theory demonstrates that ferroelectricity emerges from magnetic order. Among the *Re*MnO₃ family orthorhombic LuMnO₃ (o-LMO) and TmMnO₃ (Refs. 8–10) are of interest because the magnetic ground state is expected to be E-type, a zig-zag spin chain,¹¹ instead of a spin spiral with an electrical polarization of the order of 0.1 μC/cm² which is much larger compared to values known for TbMnO₃.^{9,12} However, the orthorhombic phase is metastable under ambient pressure because the smaller ionic radius of Lu and Tm leads to a larger distortion in the MnO₆ octahedra, thereby favoring a hexagonal structure instead. Using pulsed laser deposition (PLD), the stabilization of the orthorhombic phase can be accomplished by growing epitaxial thin films of high crystalline quality. In addition, strain induced by epitaxial growth can result in distortions in the crystal lattice, particularly in the MnO₆ octahedra. This approach enables to study the correlation between magnetism and Mn orbital ordering also as a function of growth induced strain. In this work, we investigate the Mn 3*d* states in bulk and thin film samples of o-LMO using x-ray absorption spectroscopy (XAS) of the Mn-*K*-edge at the *K*_{α1,2} fluorescence line. The experimental spectra are compared to the *ab initio* simulations using the FEFF8.4 code.^{13,14}

Samples investigated are orthorhombic LuMnO₃ bulk and thin film specimens together with an orthorhombic TbMnO₃ (o-TMO) bulk sample to obtain a comparison between the different rare earth elements. The o-LMO bulk sample was prepared using a high pressure synthesis as described in Ref. 15. The LMO thin film sample is grown on a (1–10)-oriented YAlO₃ (YAO)¹⁶ single crystalline substrate (*a* = 5.18, *b* = 5.31, *c* = 7.35 Å) at *T*_S = 760 °C by PLD (*λ* = 248 nm) with a laser fluence *F* = 2.5 J/cm².¹⁷ The film thickness used for this study is ~60 nm. To provide more atomic oxygen for the film growth, the laser was synchronized with a gas pulse to

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FIG. 1. (a) (1-10) θ -2 θ diffraction pattern of a ~ 60 nm LMO film grown on a (110)-oriented YAO substrate. The (1-10) LMO bulk position is indicated (dashed line); (b) reciprocal space map around the (2-21) reciprocal lattice point for the o-LMO film.

inject N_2O into laser induced plasma (in O_2 background: $p=0.2$ mbar).¹⁸ For the thin film preparation a stoichiometric sintered ceramic target of hexagonal LuMnO_3 (h-LMO) is used, which was prepared by conventional solid-state synthesis.

Neutron powder diffraction patterns of the bulk o-LMO sample (space group $Pbnm$) were measured at the HRPT/SINQ instrument at the Paul Scherrer Institute. The subsequently refined structural parameters obtained at 2 K are $a=5.19$, $b=5.78$, and $c=7.30$ Å.¹⁰ Compared to the bulk o-TMO ($a=5.30$, $b=5.86$, and $c=7.40$ Å), the lattice distortion is increased in o-LMO with a decrease in the Mn-O-Mn bond angle from 145.1° for Tb to 140.3° for Lu due to the smaller Lu radius.^{19,20} It is interesting to note that the differences observed in the calculated XAS spectra are independent of structural data obtained at room temperature or at 2 K. The crystalline structure of the as-grown films was characterized by triple-axis x-ray diffraction (XRD) technique, employing a Seifert diffractometer, and Cu $K\alpha$ radiation. X-ray scans confirm that o-LMO films are single phase, untwinned, and grown with a (1-10)-orientation with respect to the substrates. In the case of o-LMO thin film, Laue oscillations are observed around the out-of-plane (1-10) film peak as shown in Fig. 1(a) indicating a high coherence of the film lattice planes. Combining the (2-21) reciprocal space

mapping (RSM) (Fig. 1(b)) with the (2-20), (4-20), and the (3-20)-RMS, the film lattice parameters were determined to: $a=5.18$, $b=5.64$, and $c=7.36$ Å. This indicates that the film lattice is stretched along the c -axis and compressively strained along the [110] direction.

To probe the electronic structure, Mn K -edge x-ray absorption spectroscopy of the o-TMO and o-LMO specimens was performed at the SuperXAS/SLS beamline at the Paul Scherrer Institute. MnO and MnO_2 pellet samples were prepared together with a h-LMO polycrystalline sample as references using the same experimental setup. All spectra were recorded using a Johann-type x-ray emission spectrometer²¹ in the partial fluorescent yield (PFY) mode with an energy resolution of 1 eV, as measured with the elastically scattered radiation.²¹

The PFY at the Mn $K_{\alpha 1,2}$ fluorescence line was measured across the Mn K -edge for the polycrystalline o- LuMnO_3 sample. The obtained x-ray absorption near edge spectrum (XANES) is plotted in Fig. 2(a) along with the spectra of MnO, MnO_2 and h- LuMnO_3 with formal valences +2, +4, and +3, respectively. All the spectra comprise the same four regions: the pre-edge P , the shoulder A close to the absorption edge, the white line B , and the feature C in the higher energy region as marked in Fig. 2(a). An energy shift of the edge shoulder A with increasing valences is observed from Mn(+2) to Mn(+4). Similar edge shifts were also observed in other Mn compounds.²² Although having the same edge positions, orthorhombic and hexagonal LuMnO_3 show very different XANES spectra, especially in the pre-edge regions due to their different manganese coordination geometries of MnO_6 octahedra and MnO_5 trigonal bipyramids,²³ as well as the corresponding crystal field splitting and orbital hybridizations.²⁴

A superposition of the PFY Mn K -edge spectra of both bulk o-TMO and o-LMO samples is shown in Fig. 2(b). As expected, their overall spectral shapes show an apparent resemblance due to the same crystal structure and Mn coordination geometry (MnO_6). The white lines B in both spectra arise from the $1s$ to $4p$ Mn dipole transitions, and the shoulders A can be attributed to the hybridization between Mn $4p$ and Re $5s$ orbitals.²³ However, comparing the positions of the white lines B and the features C , respectively, shifts of ~ 1 and ~ 3 eV toward higher energies are observed for o-LMO, which are related to the larger distortion of MnO_6 induced by the decrease in the size of the Re -ion. Similar spectral shifts resulting from a smaller rare earth element were also observed in the Mn K -edge measurements of ferroelectromagnetic hexagonal ScMnO_3 compared to hexagonal YMnO_3 .²⁵

Comparing the pre-edge regions of the o-TMO and o-LMO spectra (inset of Fig. 2(b)), a triplet consisting of an intense peak and two overlapping smaller peaks is observed in the o-LMO spectrum whereas only two peaks are distinguishable for o-TMO. To verify and understand the spectral differences, simulations without polarization dependence have been performed using the FEFF8.4 code for both materials (Fig. 2(c)). The FEFF calculations well reproduced the overall shapes, the edge positions, and the shifts of the white line B and of feature C between o-LMO and o-TMO. However, in the pre-edge regions energy shifts of ~ 3 eV are

FIG. 2. (a) Mn K -edge XANES spectra at room temperature of polycrystalline MnO, MnO₂, h-LuMnO₃, and o-LuMnO₃ recorded at the $K_{\alpha 1,2}$ fluorescence line. (b) Comparison between the experimental spectra of the polycrystalline bulk o-TbMnO₃ and o-LuMnO₃ samples. (c) Comparison between the FEFF simulations of polycrystalline bulk o-TbMnO₃ and o-LuMnO₃. The pre-edge regions are magnified in the insets of (b) and (c).

observed between the experimental and simulated spectra of both o-TMO and o-LMO. Consistent with the experimental data, the simulated pre-edge of o-LMO also reveals a triplet whereas o-TMO shows a doublet only (inset Fig. 2(b)). Since both dipole and quadrupole transitions are included in the calculations for o-TMO and o-LMO, the results suggest that the o-LMO pre-edge could have the same electronic origin as o-TMO. Thus, the o-LMO pre-edge features can also be

considered to be a mixture of the quadrupole $1s$ - $3d$ transition and the off-site dipole transition as a result of hybridization between $4p$ and $3d$ states of neighboring Mn atoms like in o-TMO.²³ However, due to the larger MnO₆ distortion in o-LMO, the orbital hybridization between neighboring Mn atoms could be correspondingly altered and thus result in the onset of the third peak in the pre-edge region. To investigate the structural origin of the o-LMO pre-edge, XANES measurements with different polarizations directions were performed on the ~ 60 nm o-LMO film.

Taking advantage of the untwinned ~ 60 nm thick (1–10) o-LMO thin film, polarized PFY XAS measurements have been performed for $E \parallel [001]$ (c -axis) and $E \parallel [110]$ (in the ab plane) by rotating the sample. Both polarized measurements (Fig. 3(a)) demonstrate that the spectra of the thin film consist of the same regions as the powder sample, i.e., the pre-edge, the shoulder A close to the edge, the white line B and the feature C in the higher energy region. Comparing both spectra, a significant anisotropy is found along $[001]$ and $[110]$. With $E \parallel [001]$, both the white line B and the feature C are shifted about 1 eV towards higher energy compared to the corresponding features with $E \parallel [110]$. Furthermore, the white line

FIG. 3. (a) Mn K -edge XANES spectra of the ~ 60 nm o-LMO epitaxial film were measured at room temperature for polarizations $E \parallel [110]$ and $E \parallel [001]$. The inset shows the magnified pre-edge features. (b) FEFF simulations using the crystallographic data of the bulk o-LMO sample for $E \parallel [110]$ and $E \parallel [001]$. The simulated pre-edges are shown on a larger scale in the inset.

B is sharper and has a slightly lower intensity with $E \parallel [001]$ than with $E \parallel [110]$, whereas the feature *C* is broader and has a higher intensity. This polarization dependence arises from the anisotropic Mn–O bonding and Mn orbital ordering along the *c*-axis and the $[110]$ direction in the *ab*-plane. The same polarization dependence of the spectral shape and position is reproduced by FEFF simulations. The discrepancy in energy shifts probably originates from the bulk FEFF calculations, thereby neglecting the strain-induced lattice distortion because it is difficult to create an accurate representation of the atom arrangements for a strained film.

In the pre-edge regions of the experimental spectra, two peaks P_1 and P_2 are resolved with nearly identical positions for $E \parallel [001]$ and $E \parallel [110]$, respectively (inset of Fig. 3(a)). In addition to these two peaks, a third peak P_3 overlapping with P_2 (marked in the inset of Fig. 3(a)) appears for $E \parallel [110]$ but is not readily distinguishable with $E \parallel [001]$. This observation suggests that the Mn atomic positions in the *ab* plane and the corresponding orbital ordering are most likely responsible for the appearance of the third peak in o-LMO pre-edge regions. FEFF simulations confirm the onset of the peak P_3 for $E \parallel [110]$ as well as the P_2 peak positions for both polarizations and the dominance of the peak P_2 for $E \parallel [001]$ (Fig. 3(b)). Contrary to the experimental data, the peak P_3 is clearly present for both polarization directions in the simulated pre-edge regions whereas the peak P_1 is hardly observable for $E \parallel [001]$. The discrepancies between the experimental and simulated spectra might shed light on the influence of the strain-induced lattice distortion on the electronic transitions. For better comparison and understanding, further polarized experiments on an o-LMO single crystal and theoretical calculations on electronic structures need to be conducted.

In summary, we report on the x-ray absorption near edge structure collected at the Mn *K*-edge in partial fluorescence yield in bulk and in strained thin film samples of o-LuMnO₃ which are compared to a bulk o-TbMnO₃ sample. Due to the reduced *Re*-ionic radius and subsequent increase in MnO₆ distortion, o-LuMnO₃ has different Mn atomic positions in the *ab*-plane and orbital ordering as compared to o-TbMnO₃. This is reflected in the x-ray near edge absorption spectra by observing a triplet structure in the pre-edge regions for o-LuMnO₃ whereas o-TbMnO₃ shows a pre-edge doublet only. From polarized measurements, there is also clear evidence of anisotropic Mn–O bonding along the *c*-axis and along the $[110]$ direction in the *ab* plane. Performing FEFF8.4 simulations confirms the presence of the pre-edge triplets including the positions of the absorption edge, the white line, and the XANES features. Since the calculated spectra seemed to be qualitatively independent of the structural phase transition taking place below T_N , room temperature measurements are considered to be sufficient to evaluate, e.g., the effect of growth induced strain or the substitution of different *Re*-ions into o-*Re*MnO₃, on the electronic structure. These measurements thus represent an approach to study Mn orbital ordering as a function of *Re*-ionic radius. The above mentioned experimental results also suggest that spectral changes in, e.g., the pre-edge region should be observable if the film strain has a compar-

able influence on the MnO₆ distortion like the substitution of a rare earth element in o-*Re*MnO₃. Further experimental and theoretical investigations on highly strained films are necessary to improve the understanding of the correlation between lattice distortions and subsequent changes to the electronic structure. These measurements could be combined with the corresponding magnetic properties at low temperatures. Consequences expected for *Re*MnO₃ thin films are, e.g., a strain induced influence on the magnetic ground state or a shift of the multiferroic transition temperature.

This work was partially supported by SNF, Project No. 200020-117642, MaNEP, and the Paul Scherrer Institute. We also thank V. Pomjakushin (PSI, NUM), U. Staub, and S. W. Huang (PSI, SLS) for technical support and fruitful discussions.

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