Available online at www.sciencedirect.com
ScienceDirect
Journal of Magnetism and Magnetic Materials 310 (2007) 813–815
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Orbital polarization and Jahn–Teller distortion of strained $La_{0.5}Sr_{0.5}MnO_3$ thin films

W.B. Wu[a,b], D.J. Huang[a,c,*], C.-M. Huang[a], C.-H. Hsu[a], C.F. Chang[a,1], H.-J. Lin[a], C.T. Chen[a]

[a]National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan
[b]Department of Electrophysics, National Chiao-Tung University, Hsinchu 30010, Taiwan
[c]Department of Physics, National Tsing Hua University, Hsinchu 30013, Taiwan

Available online 15 November 2006

Abstract

We report spectroscopic evidence for orbital-mediated phases in strained $La_{0.5}Sr_{0.5}MnO_3$ thin films by combining soft X-ray spectroscopy and synthesis of manganite thin films. Measurements of polarization-dependent soft X-ray absorption reveal that electronic states responsible for the lowest-energy excitations in C-type antiferromagnetic $La_{0.5}Sr_{0.5}MnO_3$ films have an orbital symmetry of $3z^2-r^2$, while those in A-type AFM films have an orbital symmetry of x^2-y^2. Such orbital polarizations in strained films of manganite result from a combined effect of the Jahn–Teller distortion and the electron correlations of Mn 3d electrons.

PACS: 75.70. −i; 75.25.+z; 78.70.Dm; 75.50.Ee

Keywords: Orbital ordering; Perovskite manganites; X-ray absorption

1. Introduction

Manganese oxides $A_{1-x}B_xMnO_3$ (A: the trivalent rare-earth ions, B: divalent alkaline earth ions) exhibit numerous exotic physical phenomena [1–3] which arise from the strong coupling among spin, charge, orbital, and lattice degrees of freedom in manganites [4,5]. For example, the Jahn–Teller distortion of Mn^{3+} ions in these compounds plays an important role in the underlying physics of such exotic physical phenomena [6]. Particularly the strain effect in manganites are closely related to their magnetic and transport properties [7–11].

Konishi, et al. demonstrated that magnetic and electronic phases of the epitaxial strained $La_{1-x}Sr_xMnO_3$ films can be controlled via changing the lattice parameters of substrate [8]. A small tetragonal distortion in strained thin films of $La_{0.5}Sr_{0.5}MnO_3$ grown on $SrTiO_3$ or $LaAlO_3$ can result in ferro-orbital ordering of $d_{x^2-y^2}$ or $d_{3z^2-r^2}$ and different spin structures of C-type or A-type antiferromagnetic (AFM), respectively, depending upon the value of lateral strain c/a less or greater than one. $SrTiO_3$ and $LaAlO_3$ are denoted as STO and LAO, hereafter. The spin-orbital phases can be well explained by band-structure calculations based on the local density approximation (LDA) [12]. LDA calculations, however, surprisingly predict that the e_g band of C-type AFM strained manganite films has a strong x^2-y^2 orbital character at the Fermi level rather than $3z^2-r^2$, although these films exhibit a ferro-orbital ordering of $d_{3z^2-r^2}$. Such a LDA prediction is inconsistent with the resistivity measurements that the C-type strained manganites is conductive only along the c-axis [8].

Polarization-dependent soft X-ray absorption spectroscopy (XAS), particularly its linear dichroism, provides us with a powerful means to identify the spin and orbital occupation of transition-metal oxides [13–15]. Here we

*Corresponding author. II Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.
E-mail address: djhuang@nsrrc.org.tw (D.J. Huang).
[1]Present address: II Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.

0304-8853/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.jmmm.2006.10.705

demonstrate experimentally the existence of ferro-orbital ordered states resulting from tetragonal Jahn–Teller distortion by combining techniques of soft X-ray spectroscopy and synthesis of manganite thin films. To identify the orbital character of strained $La_{0.5}Sr_{0.5}MnO_3$ thin films, we measured polarization-dependent soft X-ray absorption on $La_{0.5}Sr_{0.5}MnO_3$ thin films grown epitaxially on STO and LAO with the technique of pulsed laser deposition (PLD) [16,17].

2. Growth of epitaxial thin films

We used UV radiation of wavelength 248 nm from a KrF excimer laser to achieve the PLD growth of $La_{0.5}Sr_{0.5}MnO_3$ thin films epitaxially on STO(0 0 1) and LAO(0 0 1). During the deposition of manganite thin films, substrates were kept at 900 K in a background oxygen pressure of 10 mTorr. The thickness of $La_{0.5}Sr_{0.5}MnO_3$ thin films is 200 Å. X-ray diffraction (XRD) measurements were used to characterize the crystalline structure of $La_{0.5}Sr_{0.5}MnO_3$ thin films at the beamline 17A in the National Synchrotron Radiation Research Center (NSRRC), Taiwan with photon energy of 9.3 KeV. Fig. 1(A) shows the reciprocal-space mapping of the (1 1 3) Bragg diffraction. The diffraction spots from the substrate and the thin film have the same momentum transfer Q_{110} along the [1 1 0] direction. The XRD scans along the c-axis, i.e., the Q_{001} scan, of the (1 1 3) peaks are also plotted in Fig. 1(B). These Q_{001} scans show pronounced fringes resulting from the interference between X-rays reflected from the surface and the interface. We found that thin films exhibit tetragonal Jahn–Teller distortion with elongated and contracted Mn–O bond length along the c-axis with the values of c/a for films on LAO and STO are 1.055 and 0.982, respectively.

3. Results and discussion

We performed XAS measurements on $La_{0.5}Sr_{0.5}MnO_3$ thin films at the Dragon beamline of NSRRC by collecting the sample drain current at the sample temperature of 300 K and the photon energy resolution was 0.2 eV.

Fig. 2 shows the polarization-dependent Mn 2p XAS spectra of $La_{0.5}Sr_{0.5}MnO_3$ films on LAO and STO taken with the **E** vector of photons perpendicular ($\mathbf{E} \perp c$) and parallel ($\mathbf{E} \| c$) to the samples c-axis. Linear dichroism (LD) spectrum is defined as the difference of the absorption spectra between incident photons with **E** vector perpendicular and parallel to sample surface normal (or named c-axis). For the LAO case, if $d_{3z^2-r^2}$ is occupied, unoccupied e_g bands have an orbital polarization of $x^2 - y^2$. The multipole interaction [13] described by the Gaunt coefficient indicate that the average cross section of Mn L-edge absorption excited by photons with $\mathbf{E} \| c$ is smaller than that with $\mathbf{E} \perp c$. Fig. 2(A) illustrates that the integrated intensity of LD measurements of $La_{0.5}Sr_{0.5}MnO_3$ films on LAO taken with $\mathbf{E} \perp c$ is larger than that with $\mathbf{E} \| c$, and the LD spectrum is more or less positive throughout the L_3 and L_2 edges, thus revealing that the occupied e_g states of Mn are of $3z^2 - r^2$ symmetry. In contrast, films on STO show a polarization opposite to that of on LAO demonstrating that manganite films on STO are dominated by $d_{x^2-y^2}$ orbitals, as shown in Fig. 2(B).

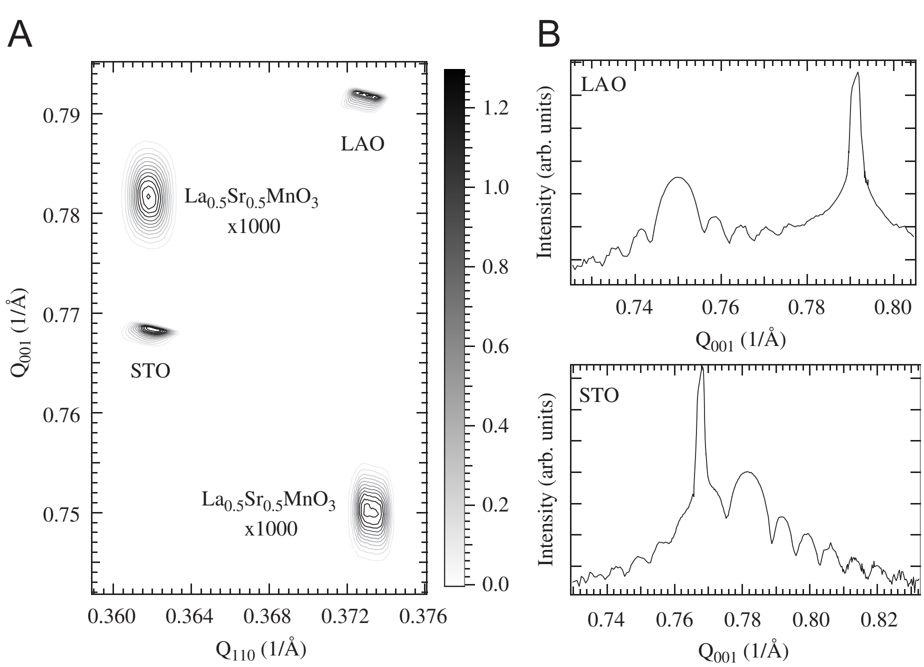

Fig. 1. (A) Left panel: the reciprocal-space mapping contour of the (1 1 3) X-ray Bragg diffraction peaks of $La_{0.5}Sr_{0.5}MnO_3$ epitaxial thin films on STO and LAO substrates. (B) Right panel: Q_{001} scans, i.e., scans with momentum transfer along the c direction of the (1 1 3) Bragg diffraction peak. Q_{110} is fixed at 0.3731 and 0.3618 $Å^{-1}$, respectively, for Q_{001} scans of thin films deposited on LAO and STO.

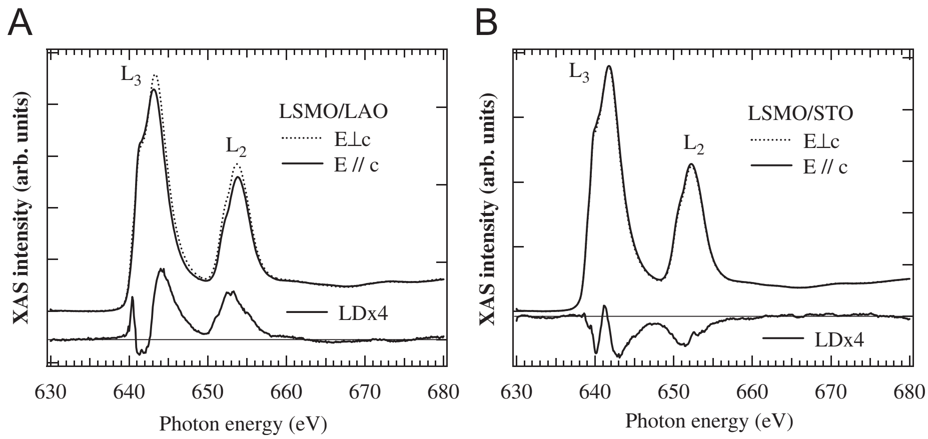

Fig. 2. LD and polarization-dependent XAS taken with $\mathbf{E}\|c$ (solid line) and $\mathbf{E} \perp c$ (broken line) of $La_{0.5}Sr_{0.5}MnO_3$ thin films grown on LAO(A) and STO(B).

We therefore show that epitaxial thin films of $La_{0.5}Sr_{0.5}MnO_3$ with laterally compressed strain exhibit an orbital polarization of $3z^2 - r^2$, while those with laterally tensile strain has an orbital polarization of $x^2 - y^2$, consistent with the predictions from previous magnetization and resistivity measurements [8]. Particularly we found that electronic states responsible for the low-energy excitations of C-type AFM $La_{0.5}Sr_{0.5}MnO_3$ films are dominated by $3z^2 - r^2$ symmetry, rather than $x^2 - y^2$ symmetry.

References

[1] Y. Tokura (Ed.), Colossal Magnetroresistive Oxides, Gordon and Breach, New York, 2000.
[2] H. Kawano, et al., Phys. Rev. Lett. 78 (1997) 4253.
[3] M.v. Zimmermann, et al., Phys. Rev. Lett. 83 (1999) 4872.
[4] J.B. Goodenough, Phys. Rev. 100 (1955) 564.
[5] Y. Tokura, N. Nagaosa, Science 288 (2000) 462.
[6] K.H. Ahn, et al., Nature 428 (2004) 401.
[7] Y. Suzuki, et al., Appl. Phys. Lett. 71 (1997) 140.
[8] Y. Konishi, et al., J. Phys. Soc. Japan 68 (1999) 3790.
[9] Yoichi Okimoto, et al., J. Phys. Soc. Japan 71 (2002) 613.
[10] Y. Wakabayashi, et al., Phys. Rev. B 69 (2004) 144414.
[11] Y. Ogimoto, et al., Phys. Rev. B 71 (2005) 060403(R).
[12] Z. Fang, et al., Phys. Rev. Lett. 84 (2000) 3169.
[13] H.B. Huang, et al., J. Phys. Soc. Japan 69 (2000) 2399; H.B. Huang, T. Jo, J. Phys. Soc. Japan 71 (2001) 3094.
[14] D.J. Huang, et al., Phys. Rev. Lett. 92 (2004) 087202.
[15] F. Iga, et al., Phys. Rev. Lett. 93 (2004) 257207.
[16] D.B. Chrisey, G.K. Hubler, (Eds.), Pulsed Laser Deposition of Thin Films, Wiley, New York, 1994.
[17] M. Kawasaki, et al., Mater. Sci. Eng. B 63 (1999) 49.