Orbital polarization and Jahn–Teller distortion of strained La$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films

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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.

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1. Introduction

Manganese oxides A$_{1-x}$B$_x$MnO$_3$ (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 is 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$_x$MnO$_3$ 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
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(001) and LAO(001). 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 A. 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 [1 1 0] direction 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.

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 (E $\perp$ c) and parallel (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$_{2,-2}$ 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 E||c is smaller than that with 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 E $\perp$ c is larger than that with 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$_{2,-2}$ orbitals, as shown in Fig. 2(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