

## Observation of strain and temperature induced changes in the band structure of thin $\text{La}_{0.8}\text{MnO}_{3-\delta}$ films

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Mn *K*-edge resonant inelastic x-ray scattering measurements were performed on films of  $\text{La}_{0.8}\text{MnO}_{3-\delta}$ . The measurements reveal that strain causes large shifts of the bands above the Fermi level. The Mn 3*d* band switches from a narrow upshifted peak at high temperature to a broad bulklike band at low temperature in ultrathin films. The strain induced switching behavior opens the possibility of tuning the transition to higher temperatures for device applications in this class of manganite materials. © 2007 American Institute of Physics. [DOI: 10.1063/1.2711779]

The  $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$  (Re=rare earth and A=Ca, Sr, Ba, etc.) mixed valence  $[\text{Mn}^{3+}(d^4, t_{2g}^3 e_g^1)/\text{Mn}^{4+}(d^3, t_{2g}^3 e_g^0)]$ , perovskite system exhibits complex and intriguing properties and an understanding of the basic physics of this material has still not been realized.<sup>1-6</sup> From a technological perspective the close coupling of the spin, lattice, and electronic properties opens a useful way to store information.

A systematic approach in understanding the fundamental parameters in manganites is attainable by utilizing thin films.<sup>7</sup> Thin films can be made with the same stoichiometry as bulk samples and can be produced for samples in which single crystals are not available. In addition, by taking advantage of the substrate induced strain, the electron, spin, and lattice coupling in these systems can be studied. Thin strained manganite films are found to exhibit insulating behavior and low saturation magnetization as the thickness of the film is reduced.<sup>8</sup>

Both ferromagnetic order and metallic conductivity can be obtained in the self-doped system,  $\text{La}_x\text{MnO}_{3-\delta}$  ( $x > 0$  and  $\delta > 0$ ). The ordering temperature can be adjusted by varying oxygen content and the La deficiency.<sup>9</sup> It is a complex system in which properties can be tuned, such as in the classic  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  system but with fewer components. In our previous studies of  $\text{La}_{0.8}\text{MnO}_{3-\delta}$  films, we found an increase in the degree of local distortion of the  $\text{MnO}_6$  octahedra with reduced film thickness by near edge x-ray absorption spectroscopy at the manganese *K* edge.<sup>10,11</sup> Bulk magnetization measurements conducted by superconducting quantum interference device (SQUID) magnetometry on 6, 30, and 160 nm thick films showed a reduction of the magnetic ordering temperature ( $T_c$ ) and magnetic saturation moment with a reduction in thickness. Films of the entire thickness range exhibit metal-like conductivity at low temperature.

Mn *K*-edge resonant inelastic x-ray scattering (RIXS) provides a method to examine the changes in the electronic structure of materials. Studies on manganites reveal weak peaks in the energy loss spectrum which appear when the incident beam is tuned above the Mn *K* edge. One can see transitions between the lower ( $\text{O } 2p + e_g^1 \uparrow$ ) and upper ( $e_g^2 \uparrow$ ) Hubbard bands, between the oxygen 2*p* and Mn 3*d* bands, and between oxygen 2*p* and La 5*d* or 4*p*–4*s* bands with increasing energy (see Ref. 12). In Fig. 1 we show a schematic of the valence band of the manganites, as developed from optical measurements,<sup>12,13</sup> indicating the positions of these bands above the Fermi energy for an insulating (a) and a metallic (b) manganite.

The RIXS method provides an approach to probe changes in the electronic structure (changes in the valence band positions, widths, and intensities) when strain from a substrate is imposed. With the advent of third generation synchrotron x-ray sources, it is becoming possible

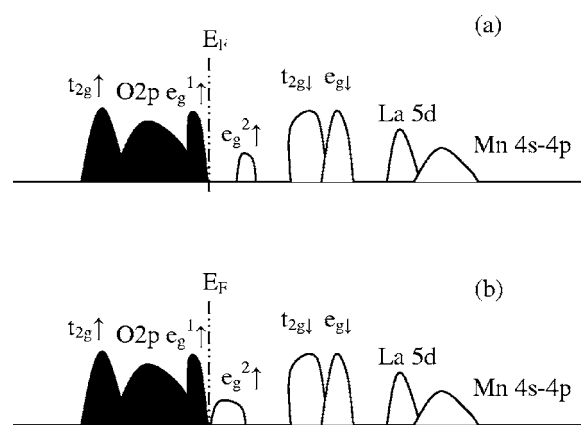


FIG. 1. Schematic of the band structure of (a) insulating and (b) metallic phases of manganites (based on optical data). (Ref. 12 and 13) Note that above the Fermi energy the bands form three distinct groups:  $e_g^2 \uparrow$ ,  $t_{2g} \downarrow / e_g \downarrow$ , and La 5*d*/Mn 4*s*–4*p* Mn.

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to carry out systematic studies of materials utilizing this low cross section process (with typical counting rate of 2–10 counts/s). Measurements on ultrathin films are now at the edge of experimental accessibility.

RIXS measurements were performed on ultrathin (9 nm) and thick (412 nm) films of  $\text{La}_{0.8}\text{MnO}_{3-\delta}$ . The measurements reveal that strain causes large shifts of the Mn 3*d* and Mn 4*p*/4*s* bands above the Fermi level. The thinnest film is found to exhibit a switch from a localized 3*d* band at high temperature to a delocalized metal band at low temperature.

Epitaxial  $\text{La}_{1-x}\text{MnO}_{3-\delta}$  ( $x \sim 0.2$ ) films were grown on (012)  $\text{LaAlO}_3$  substrates [referred to as  $\text{LaAlO}_3$  (001) by the pseudocubic designation] by metal-organic chemical vapor deposition. The reactor and the experimental procedure are described elsewhere.<sup>9</sup> Mn  $K_\beta$  high-resolution x-ray emission and x-ray absorption measurements indicate that all films have the same average Mn valence. RIXS measurements were conducted at the Taiwan BL-12XU beamline at Spring-8.<sup>14</sup> The undulator beamline utilized a Si(111) double crystal monochromator and the beam was focused to 80(V)  $\times$  120(H)  $\mu\text{m}^2$ . The measurements on the inelastic x-ray spectrometer were conducted in a closed cycle cryostat with  $q$  set at (0, 0, 2.3)  $\text{\AA}^{-1}$ . A single 4 in. Si(440) analyzer with a resolution of  $\sim 0.5$  eV was used. The resolution of the complete system was 1 eV. In the RIXS scans the incident energy was set at 6556 eV near the peak of the Mn  $K$ -edge absorption spectrum. X-ray diffraction measurements reveal 1% strain (out-of-plane lattice parameter change) in the 9 nm film compared with the 412 nm film. By SQUID magnetometry, the 412 nm film was found to have a  $T_C$  of  $\sim 270$  K with a saturation magnetization of  $3.7\mu_B/\text{Mn}$  (at 25 K) while the corresponding  $T_C$  and saturation magnetization values for the 9 nm film are  $\sim 100$  K and  $1.4\mu_B/\text{Mn}$  (at 25 K), respectively.

In Fig. 2 we show the energy loss spectrum for the 412 nm (upper panel) and 9 nm (lower panel) films measured at room temperature and 10 K. The measurements constitute a comparison of the electronic structure in the ferromagnetic metallic state and in the paramagnetic insulating state. The large shoulder on the left side is from the elastic peak. We note that no subtraction of the smooth elastic peak background is made.

In the 412 nm film, the loss resonances corresponding to the three distinct regions are evident. With temperature change the reduction of the width of the elastic peak suppresses the background. With temperature decrease there is a narrowing of the elastic peak due to the reduction of the thermal factor (reduced atomic motion). While the width of the elastic peak increases by  $\sim 30\%$  for the thick film and 80% for the thin film with increased temperature, it broadens the elastic peak by at most  $\sim 1$  eV (on the scale shown in Fig. 2) and does not affect the qualitative trends to be discussed below. Returning to Fig. 2(a), we note that the positions and shapes of the peaks labeled A ( $\sim 5$  eV), B ( $\sim 8$  eV), and C ( $\sim 12$  eV) do not change with temperature. As in the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  crystals,<sup>15</sup> the region from 4 to 10 eV in the energy loss has been found to anticorrelate with the magnetization. Hence, this film behaves as an unstrained bulk material. We associate these peaks with transition to the upper Hubbard band (lower band =  $\text{O } 2p + e_g^1\uparrow$  and upper band =  $e_g^2\uparrow$ ), the Mn 3*d* band, and La 5*d*/Mn 4*p*–Mn 4*s* bands (as in Ref. 12).

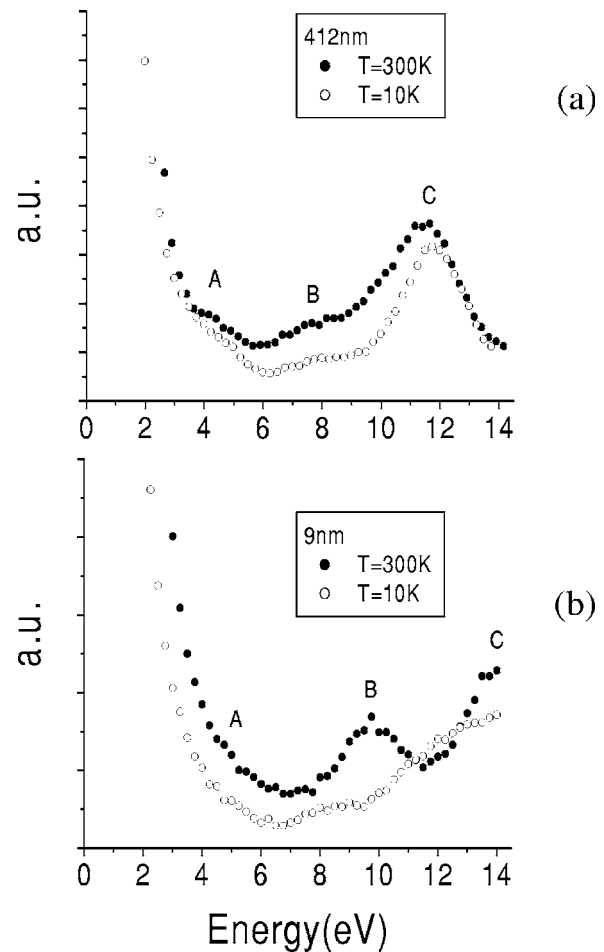


FIG. 2. RIXS (energy loss) spectra for the (a) 412 nm film and (b) 9 nm film measured at 10 and 300 K.

On the other hand, significant changes are seen in the 9 nm film (1% strained). The A, B, and C features are shifted to higher energy compared to the thick film—occurring at  $\sim 5$  eV,  $\sim 9$  eV, and above  $\sim 14$  eV, respectively. While the low temperature scan for the 9 nm film is not qualitatively different from the thick film at low temperature, the B peak is quite strong at high temperature. The main reason for the large change in amplitude of the B (oxygen 2*p* to Mn 3*d*) peak when going to high temperature ( $\sim 300$  K) is that one is very far from the ferromagnetic (FM) and metallic states ( $\sim 150$  K above the FM state). In addition, strain effects are affecting the thin films as can be seen from the low saturation magnetization. This suggests that the 3*d* band of the thin film is transformed from a highly localized band at high temperature to a broad band at low temperature.

According to a recent theoretical study,<sup>15</sup> RIXS intensity originates dominantly from one unentangled electron-hole pair excitation. Therefore, the RIXS intensity  $I(\omega)$  is given as a convolution between the hole  $[n_h(\epsilon_h)]$  and electron  $[n_e(\epsilon_e)]$  spectral functions, weighted by the densities of states  $[D^h(\epsilon_h), D^e(\epsilon_e)]: I(\omega) \sim \sum_{\epsilon_e, \epsilon_h} n_e(\epsilon_e) n_h(\epsilon_h) \delta(\omega - \epsilon_e + \epsilon_h) D^e(\epsilon_e) D^h(\epsilon_h)$ . Furthermore, this study demonstrated a strong asymmetry between  $n_e(\epsilon_e)$  and  $n_h(\epsilon_h)$ . The 1*s* core hole created by the incoming x ray is screened by a localized electron, the excitation of which implies that  $n_e(\epsilon_e)$  distributes over the whole momentum space in the unoccupied bands. The hole left behind is in a delocalized minimum kinetic energy state, which means that  $n_h(\epsilon_h)$  is concentrated near the Fermi en-

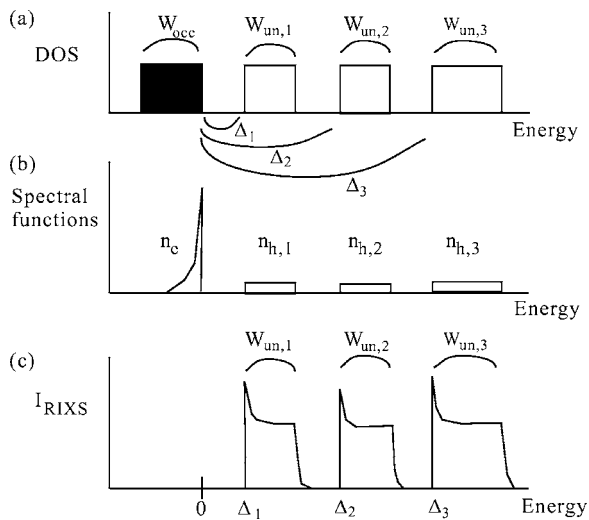


FIG. 3. Schematic drawings of (a) density of states of an occupied band with width  $W_{\text{occ}}$  and three unoccupied bands with widths  $W_{\text{un},1}$ ,  $W_{\text{un},2}$ , and  $W_{\text{un},3}$ , (b) spectral functions for the electron and hole excitations, and (c) expected RIXS intensity.

ergy in the occupied band. Therefore, the energy where the RIXS peak starts corresponds to the gap between the occupied and unoccupied bands. The width of the RIXS peak reflects mainly the width of the unoccupied band, although the occupied bandwidth also contributes to the RIXS peak width as the gap size increases.

We generalize the findings in Ref. 16 to our results for  $\text{La}_{1-x}\text{MnO}_{3-\delta}$  ( $x \sim 0.2$ ) and consider the density of states shown in Fig. 3(a). The asymmetric electron and hole spectral functions would be similar to the ones shown schematically in Fig. 3(b), and the three measured RIXS peaks can be modeled as illustrated in Fig. 3(c). The energies where the RIXS peaks start correspond to the energy gaps  $\Delta_1$ ,  $\Delta_2$ , and  $\Delta_3$  shown in Fig. 3(a). The RIXS peak widths are close to the unoccupied bandwidths,  $W_{\text{un},1}$ ,  $W_{\text{un},2}$ , and  $W_{\text{un},3}$ . Therefore, the change in the width of peak B mentioned above signifies the change in the width of the unoccupied Mn 3d bands, rather than the occupied oxygen 2p bands. The large shift of peak C implies the shift of the La 5d/Mn 4s–Mn 4p bands. Comparison of Figs. 2(a) and 2(b) reveals that the cooling in the thin film restores the bulklike features in peak B but not in peak C. Only the energy where peak C starts becomes similar to that in the bulklike thick film, 10 eV. Such behavior of peak C can be related to the complexity of the La 5d/Mn 4s–Mn 4p bands. Some part of this band (e.g., Mn 4s–Mn 4p band) is strongly influenced by the delocalization of the Mn 3d electrons (e.g., through the on-site Coulomb interaction) and shifted downward upon cooling, resulting in a gap energy similar to that in the bulk. In contrast, another part of the band (e.g., La 5d) is determined mainly by the substrate induced strains and unaffected by the cooling, so that the whole shape of peak C in the thin

film differs from that in the bulk at low temperatures. The results demonstrate that the RIXS can provide useful information on the electronic structure changes induced by strains and cooling.

The ability to tune electronic density of states with strain may be useful for switching devices. From a fundamental perspective a broader range of combined temperature dependent RIXS and structural measurements is needed to fully understand the nature of the electronic structure transition seen in these films.

In summary, RIXS measurements were performed on ultrathin (9 nm) and thick (412 nm) films of  $\text{La}_{0.8}\text{MnO}_{3-\delta}$ . The measurements reveal that strain causes large shifts of the bands above the Fermi level. The Mn 3d band switches from a narrow upshifted peak at high temperature to a broad bulklike band at low temperature. The strain induced switching behavior opens the possibility of tuning the transition to higher temperatures for device applications.

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