

# Strain-induced change in local structure and its effect on the ferromagnetic properties of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ thin films

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We have used high-resolution extended x-ray absorption fine-structure and diffraction techniques to measure the local structure of strained  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  films under compression and tension. The lattice mismatch strain in these compounds affects both the bond lengths and the bond angles, though the larger effect on the bandwidth is due to the bond-length changes. The popular double exchange model for ferromagnetism in these compounds provides a correct qualitative description of the changes in Curie temperature  $T_C$ , but quantitatively underestimates the changes. A microscopic model for ferromagnetism that provides a much stronger dependence on the structural distortions is needed. © 2008 American Institute of Physics. [DOI: 10.1063/1.3011031]

Epitaxial strain in thin films is often used to modify a material's physical properties and improve device performance. For example, biaxial strain can introduce bond-length and bond-angle distortions in semiconductor alloys,<sup>1–4</sup> which greatly affect their performance in real applications. Room temperature ferroelectricity has been induced by lattice strain in  $\text{SrTiO}_3$  thin films, a material that is not ferroelectric in the bulk.<sup>5,6</sup> Enhanced magnetoresistance has been achieved in  $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$  thin films at room temperature,<sup>7</sup> which makes it a potential candidate for magnetic devices and sensors. The modification of physical properties using strain is also an important tool for understanding the physics of correlated electron materials. One longstanding question in the field is the origin of ferromagnetism in several poorly conducting transition-metal oxides. The most popular model has been Zener's double exchange (DE) mechanism.<sup>8</sup> In this paper we report results comparing the Curie temperature with detailed structural measurements in strained films of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (LSCO). While the predictions appear qualitatively correct, they do not quantitatively predict the correct dependence on lattice parameter and, therefore, bandwidth. Thus, either another mechanism or a modification to DE is needed.

The perovskite, transition-metal oxide that has been most studied as a function of strain is the colossal magnetoresistive manganites.<sup>9</sup> The strain has been induced in several ways in manganites including films. The analysis of these experiments has examined how strain has mediated the ferromagnetic coupling via modification of the bandwidth  $W$ .<sup>8,10</sup> In the tight-binding model, the bandwidth  $W$  depends on the overlap integrals between the Mn  $3d$  and O  $2p$  orbitals such that  $W \propto d^{-3.5} \cos \omega$ ,<sup>11,12</sup> where  $d$  is the Mn–O bond length,  $\omega = (180^\circ - \phi)/2$  is the tilt angle, and  $\phi$  is the Mn–O–Mn bond buckling. A decrease in the lanthanide ion radius by chemical substitution leads to a reduction in  $T_C$  that has been attributed to an increase in the Mn–O–Mn bond angle with little change in the Mn–O bond length.<sup>13,14</sup> The opposite case is that compressive hydrostatic pressure increases  $T_C$  due to a reduction in the Mn–O bond length with little decrease in the Mn–O–Mn bond angle.<sup>15</sup> However, for film studies no full consensus has been reached. Yuan<sup>16</sup> proposed

that tensile strain primarily increases the Mn–O–Mn bond angle to explain the enhancement of  $T_C$ . Miniotas *et al.*<sup>17</sup> reported that the Mn–O bond length remains fixed, while the Mn–O–Mn bond angle accommodates the strain. Similar behavior was assumed in other work.<sup>18</sup> However, an x-ray absorption spectroscopy (XAS) study indicated an energy shift at Mn  $K$ -edge in strained  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  thin films, implying a variation in Mn–O bond length.<sup>19</sup> The system of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  is of great interest in its own right, with a wide variety of applications.<sup>20–22</sup> Recent studies have shown that strain can directly alter the ferromagnetic exchange coupling energy.<sup>23</sup> The details of just how this happens require more exact measurements of the local structure as reported here using extended x-ray absorption fine structure (EXAFS).

LSCO films with a thickness of 22 nm were epitaxially grown by a pulsed laser deposition technique on  $\text{LaAlO}_3$  (LAO) and  $\text{SrTiO}_3$  (STO) substrates. X-ray diffraction (XRD) using a four-circle diffractometer confirmed the epitaxy of the films and indicated the absence of impurity phases or grains with other orientations. We determined both the in-plane and out-of-plane lattice strains by  $\epsilon = (a_f - a_b)/a_b$ , where the  $a_f$  and  $a_b$  ( $\approx 3.834 \text{ \AA}$ ) are the lattice constants for LSCO film and bulk, respectively, as measured by XRD. The field-cooled dc magnetic properties were measured using a superconducting quantum interference device magnetometer with the applied field direction parallel to the sample surface. High resolution EXAFS experiments were conducted on the Co  $K$ -edge at room temperature using the National Institute of Standards and Technology beamline X23A2 at the National Synchrotron Light Source, Brookhaven National Laboratory. The absorption data were collected in two orientations, with the polarization vector  $\vec{\epsilon}$  of the synchrotron radiation aligned either parallel or perpendicular to the sample surface. The x-ray absorption spectrum from finely ground LSCO powder measured in transmission was used as the EXAFS phase and amplitude standard to experimentally determine the Co–O bond lengths within the films.

Figure 1 shows the field-cooled magnetization curves  $M(T)$  for LSCO thin films grown on STO and LAO substrates, respectively. The film on STO has an in-plane lattice constant of  $3.891 \pm 0.002 \text{ \AA}$  and an out-of-plane lattice constant of  $3.778 \pm 0.001 \text{ \AA}$  to give an in-plane tensile strain of

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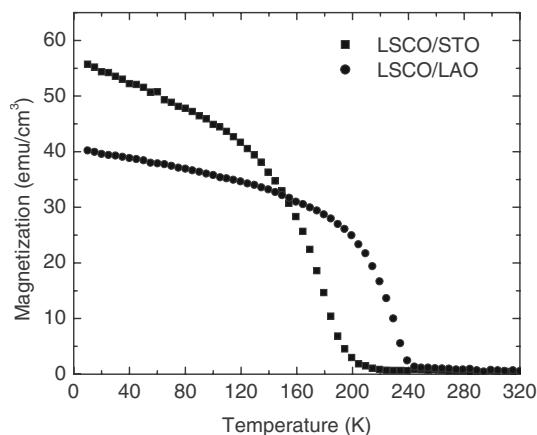


FIG. 1. Temperature dependence of field-cooled magnetization with applied field  $H=100$  Oe for LSCO films on STO and LAO substrates.

+1.49%, an out-of-plane compressive strain of  $-1.46\%$ , and  $T_C$  of 198 K. The film on LAO has an in-plane lattice constant of  $3.808 \pm 0.004$  Å and an out-of-plane lattice constant of  $3.869 \pm 0.002$  Å to give an in-plane compressive strain of  $-0.68\%$ , an out-of-plane tensile strain of  $+0.91\%$ , and  $T_C$  of 241 K. Errors in lattice constants were estimated based on the standard deviation in the peak width from fits to the XRD peaks. These  $T_C$  values should be compared to the expected, unstrained value for  $T_C$  of 229 K determined in our previous work, which is itself reduced from the bulk value of 250 K due to the finite size effect.<sup>23,24</sup> The magnetization at low temperature is larger for the film on STO than it is for the film on LAO. While this might indicate a change in the total ordered moment, it is not possible to draw a firm conclusion from such low field data alone. EXAFS allows for a precise measurement of the Co–O bond length. Figure 2 displays the  $R$ -space Fourier transforms (FTs) of the Co  $K$ -edge EXAFS spectra for the polarization vector parallel and perpendicular to the surface normal for the two LSCO films, along with the spectra for a reference powder of LSCO. The peak in the FT near  $1.45$  Å corresponds to the backscattering from the first coordinate neighbor O atoms. The peak between 3 and 4 Å

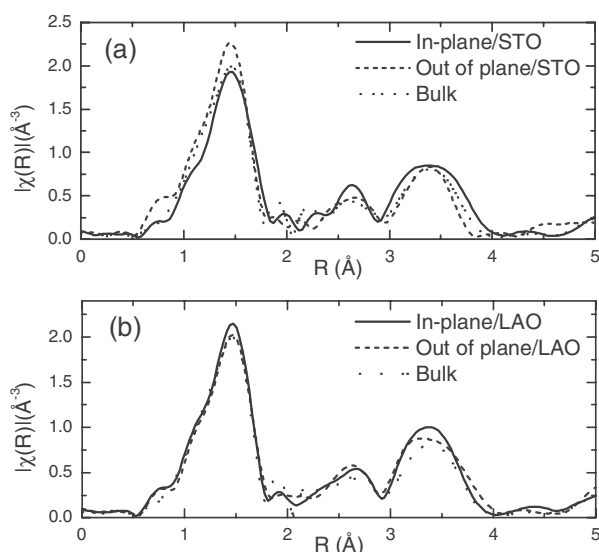


FIG. 2. Magnitude of the FTs of the  $k^2$ -weighted Co  $K$ -edge EXAFS with the polarization vector of the synchrotron radiation aligned in plane and out of plane for LSCO thin films grown on (a) STO and (b) LAO substrates, respectively. For comparison, data of LSCO powder as a standard are also shown.

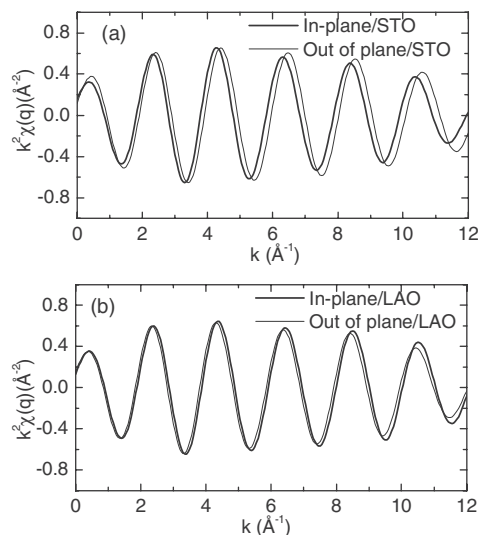


FIG. 3. Inverse FT for the filtered first-shell Co–O contribution to the Co  $K$ -edge EXAFS for LSCO films grown on (a) STO and (b) LAO substrates, respectively.

in Fig. 2 consists of the scattering paths of second shell Co–La and Co–Sr and third shell Co–Co along with multiple scattering variants such as Co–O–Co.

Figures 3(a) and 3(b) show the inverse FT of the first-shell filtered EXAFS for the two LSCO films that correspond to the first-shell Co–O bond. The difference in the oscillation frequency between in-plane and out-of-plane is due to the difference of the Co–O bond lengths. For the film on STO, the in-plane frequency is smaller than that of out of plane because the Co–O bond length is longer for in plane. The situation is reversed for the film on LAO. Clearly, the Co–O bond lengths adjust to accommodate the strain, which is consistent with the XAS results of strained Mn–O bond length in manganite films.<sup>19</sup> In order to quantitatively determine these bond lengths, the Co–O radial shell for thin films was modeled with the EXAFS phase and amplitude functions obtained from the bulk LSCO powder. Assuming that the Co–O bond length for powder is  $1.915$  Å, we find the bond length of  $d_{in}=1.936 \pm 0.009$  Å and  $d_{out}=1.899 \pm 0.013$  Å for the LSCO thin film on STO, while for the film on LAO, the bond lengths are  $d_{in}=1.910 \pm 0.010$  Å and  $d_{out}=1.925 \pm 0.008$  Å, respectively, where  $d_{in}$  and  $d_{out}$  denote the in-plane Co–O bond length and the out-of-plane bond length, respectively. Alternatively, fitting the out-of-plane data with the in-plane data for each film, we arrive at the following bond-length shears:  $d_{in}-d_{out}=0.038 \pm 0.009$  Å for the LSCO film on STO substrate and  $d_{in}-d_{out}=-0.016 \pm 0.004$  Å for the film on LAO substrate, respectively. Errors in bond length were estimated by the spread of distances that resulted in a doubling of the  $\chi^2$  error.

An examination of the relative modification of Co–O bond length and lattice constant allows us to assess the change of bond angle induced by strain. Figure 4 plots the relative changes of the Co–O bond length from EXAFS along with the relative changes of the lattice constant from XRD in both directions for both samples. The difference in scale for the two vertical axes means that if all of the strain were taken up in the bond length, the two data points would coincide. If all of the strain were accommodated by the bond angle,  $\Delta d$  would be fixed at zero. Clearly both are changing. The inset in Fig. 4 shows the geometrical relation

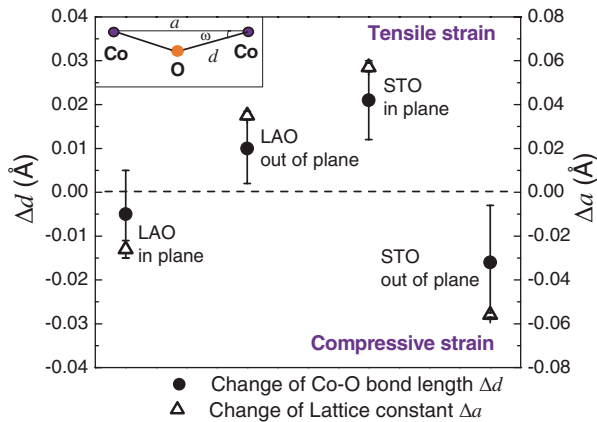


FIG. 4. (Color online) Changes of Co–O bond length and lattice constant measured with EXAFS and XRD experiments, respectively. Error bars are as indicated. The inset shows the geometrical relation between the bond length  $d$ , lattice constant  $a$ , tilt angle  $\omega$ , and bond angle  $\phi$ , which is used to calculate the relative distortions.

between the bond length  $d$ , lattice constant  $a$ , and tilt angle  $\omega$  such that  $a=2d \cos \omega$ , valid for a nearly cubic system. Assuming small distortions, we derive the change of the tilt angle in strained thin films,  $\Delta\omega=(2\Delta d-\Delta a)/2d\omega$  and  $\Delta\phi=-2\Delta\omega$ . Note that bulk LSCO has the average bond angle  $\phi$  approximately equal to  $168^\circ$ .<sup>25</sup> For the film on STO, we calculate that the in-plane bond angle  $\phi$  increases to  $172.3^\circ \pm 2.6^\circ$ , while out-of-plane  $\phi$  decreases to  $161.2^\circ \pm 3.7^\circ$ . Similarly, for the film on LAO, in-plane  $\phi$  decreases to  $163.5^\circ \pm 2.8^\circ$ , while out-of-plane  $\phi$  increases to  $172.3^\circ \pm 2.3^\circ$ . Using the bandwidth equation, the full change in the in-plane bandwidth for the film on LAO compared to the film on STO is +3.9%. Consideration of the bond angle alone would give a change of -0.8% while consideration of bond length alone would give a change of +4.7%. While both factors clearly matter, the bond-length change is the dominant effect. This is contrary to the assumptions generally used in literature on strained oxide films, and, in particular, it is different from results reported for manganite films.<sup>16–18</sup>

The detailed structural information and the measured Curie temperatures allow us to examine what models are appropriate for describing the magnetism in LSCO. The most popular model for magnetism in these materials, is the DE model. In this model, the exchange energy  $J$  is proportional to the electron transfer integral  $t$  or bandwidth  $W$ . Generally, one finds  $T_C \propto J$ . As an extreme but mathematically simple case, we can consider that  $T_C$  is controlled only by the in-plane  $J$ . Under this assumption we find that the total percentage change in bandwidth from films on LAO to those on STO is  $\Delta W \approx 3.9\%$ , considerably smaller than the change of  $T_C$  ( $\approx 19.2\%$ ). Therefore, the dependence  $J \propto W$  is not large enough to quantitatively account for the variation observed, with a stronger dependence like  $J \propto W^2$  needed. Another mechanism must either supplement or replace the DE model. For the manganites, an additional possibility discussed by Millis *et al.*<sup>26</sup> is a static Jahn–Teller (JT) distortion occurring at the transition.<sup>13</sup> That appears not to be operative for LSCO as there is only a small change in resistivity at  $T_C$ , and no sudden change in the JT distortion. A possible alternative may be found in some early work by Goodenough.<sup>27</sup> He proposed that the interaction between  $\text{Co}^{4+}$  and  $\text{Co}^{3+}$  could be of a modified superexchange type, which is regarded as an

alternative explanation of ferromagnetism in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ . Superexchange interactions involve virtual hopping processes and one expects a larger dependence of the exchange energy  $J$  on the bandwidth  $W$ , typically  $J \propto W^2$ , and thus might better match the observation reported here. However, superexchange interactions are typically considered to involve well-localized electrons and thus usually appear for insulators. A theoretical development explicitly tailored for LSCO will be necessary to fully understand the microscopic origin of magnetism in these compounds.

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