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### **Publication Date**

2009-03-04

Ferromagnetism in tetragonally distorted LaCoO<sub>3</sub> thin films

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## ABSTRACT

Thin films of epitaxial  $\text{LaCoO}_3$  were synthesized on  $\text{SrTiO}_3$  and  $(\text{La, Sr})(\text{Al, Ta})\text{O}_3$  substrates varying the oxygen background pressure in order to evaluate the impact of epitaxial growth as well as oxygen vacancies on the long range magnetic order. The epitaxial constraints from the substrate impose a tetragonal distortion compared to the bulk form. X-ray absorption and x-ray magnetic circular dichroism measurements confirmed that the ferromagnetism arises from the Co ions and persists through the entire thickness of the film. It was found that for the thin films to show ferromagnetic order they have to be grown under the higher oxygen pressures, since a decrease in oxygen deposition pressure alters the film structure and suppresses ferromagnetism in the  $\text{LaCoO}_3$  films. A correlation of the structure and magnetism suggests that the tetragonal distortions induce the ferromagnetism.

Lanthanum cobalt oxide  $\text{LaCoO}_3$  (LCO) is a perovskite oxide material that has been intensely studied throughout recent decades. Initial interest was based on its applications as a catalytic material for the fuel cell industry but research today focuses on the unique spin transition and ground states found in the bulk material. Initial theoretical studies on the nature of the transition in the doped system  $(\text{La} - \text{Sr})\text{CoO}_3$  were introduced in the 1960s.<sup>1,2</sup> Since then, there have been many experimental and theoretical studies investigating the spin behavior, but there has yet to be a consensus on the details of the higher temperature spin ground state of this material.<sup>3, 4, 5, 6, 7, 8, 9, 10</sup>

There is consensus that below 100 K, bulk LCO is diamagnetic and the Co ions are in a low spin (LS) ground state. Above 100 K, LCO undergoes a cooperative spin transition to a paramagnetic higher spin state. However, the nature of these higher spin states is unclear. In particular, two distinct spin states have been proposed, the intermediate spin (IS) with  $S=1$ <sup>7, 9, 10</sup> and the high spin state (HS) with  $S=2$ .<sup>3, 5, 6, 8</sup> In any case, in the bulk, the Co spins never exhibit long-range ordering, and at best only very weak and possibly dynamic ferromagnetic and antiferromagnetic correlations have been reported.<sup>4, 11</sup>

Only recently has LCO been grown in thin film form by Fuchs *et al.* Surprisingly, the LCO films, grown on  $\text{SrTiO}_3$  (STO),  $\text{LaAlO}_3$  (LAO) and  $(\text{La}, \text{Sr})(\text{Al}, \text{Ta})\text{O}_3$  (LSAT) substrates exhibit a ferromagnetic ground state below 85 K not observed in the bulk.<sup>12</sup> Fuchs *et al.* proposed Jahn Teller distortions induced by the epitaxial strain as the origin of the cooperative phenomena.<sup>12</sup> There have also been purely theoretical studies suggesting a route to the stabilization of the ferromagnetic ground state in LCO. For example, Rondinelli and Spaldin predict a ferromagnetic ground state for LCO distorted from the bulk;<sup>13</sup> however, their model also predicts metallic conductivity while experimentally our ferromagnetic LCO thin films are

insulating. Thus, the key elements of the ferromagnetism in LCO thin films are still not fully understood and warrant further study.

To explore the ferromagnetic ground state of LCO in detail, we performed a systematic investigation of LCO thin films grown on STO and LSAT substrates varying the background pressure during deposition in order to probe the role of epitaxial lattice distortions as well as oxygen vacancies in the long range magnetic ordering. We find that, regardless of oxygen deposition conditions and in contrast to the bulk form, all films are tetragonally distorted due to heteroepitaxial growth on to the substrate. Moreover, we observe that the ferromagnetic order is not just a surface or impurity effect, but arises from the Co ions distributed throughout the entire films. We also see that increased oxygenation during the deposition is critical to the magnetism since a lower oxygen deposition pressure alters the structure and suppresses ferromagnetism in the LCO films.

## **Experiment**

LCO films were grown using pulsed laser deposition (PLD) on STO (001), Nb:STO (001) and LSAT (001) substrates. Bulk LCO can be characterized by a pseudo-cubic lattice parameter of 3.80Å which is similar to the 3.87Å LSAT and 3.90Å STO cubic lattice parameters. For the PLD growth, a KrF excimer laser operating at 248 nm was pulsed at 3Hz on a rotating target at an energy density of 1.1-1.2 J/cm<sup>2</sup>. The laser was pulsed at a rate of 3 Hz at a stoichiometric ceramic target of LaCoO<sub>3</sub> to grow films ranging from 20- 90 nm thick in an oxygen background pressure between 10 mTorr to 320 mTorr. The substrates were held at 700°C during deposition.

Stoichiometry and thickness of the deposited films were confirmed by Rutherford Backscattering (RBS) measurements. All films had a La:Co ratio of 1:1 to within the 5% accuracy inherent to RBS. Oxygen stoichiometry could not be ascertained with similar accuracy

due to the smaller stopping cross-section of the oxygen. Surface morphology of the films was measured using a Atomic Force Microscopy in tapping mode. Structural characterization was performed on a Panalytical X'Pert MRD four - circle X-ray diffractometer with a Cu K $\alpha$  source and 4- bounce monochromator in rocking curve geometry. Standard  $\theta$ -2 $\theta$  scans were taken to obtain information on the crystalline quality and phase purity of the thin films. Reciprocal space maps were taken to confirm in plane lattice strain.

X-ray absorption (XA) spectroscopy and x-ray magnetic circular dichroism (XMCD) measurements at the Co  $L_{2,3}$  edges allow us to probe the valence state and magnetic order of Co. Both XA and XMCD are element specific, surface sensitive techniques. These measurements were performed at beamlines 6.3.1 and 4.0.2 of the Advanced Light Source. LCO/Nb:STO samples were used for low temperature measurements in order to overcome charging effects caused by the low conductivity of the thin films at cryogenic temperatures. The XA and XMCD measurements were performed at 15 K at 30° grazing incidence using elliptically polarized x-rays. XMCD spectra were measured in a magnetic field of  $\pm 0.5$  T applied collinear to the x-ray beam. Bulk magnetization measurements for the films were carried out using a Quantum Design Magnetic Property Measurement System (MPMS) equipped with a Superconducting Quantum Interference Device (SQUID). Magnetization versus temperature measurements were obtained in an applied field of 0.2 T after field cooling the samples. Magnetization versus applied field measurements were performed at 5 K with the applied field aligned in the plane of the sample.

## **Results and Discussion:**

Atomic Force Microscopy measurements revealed smooth surface morphology with root-mean-squared (rms) roughness ranging from 0.323 nm to 1.69 nm. The lower oxygen pressure films showed the lowest rms roughness (less than one unit cell) and terraces associated with the

substrate miscut. At higher oxygen pressures, the rms roughness increased to the order of 2 unit cells. The thicker films (~90nm) grown on STO substrates tended to crack and buckle along crystallographic directions. Films grown on LSAT substrates did not exhibit this cracking behavior, but were rougher than 1 nm.

X-ray diffraction measurements in the  $\theta$ - $2\theta$  geometry showed the single phase (001) family of reflections for the LCO films and substrate. Rocking curves of the LCO film peaks had FWHM on the order of  $0.1^\circ$ , thus indicating little mosaic spread. In-plane lattice parameters were determined from reciprocal lattice maps (Fig. 1) taken on the (103) peak of LCO films. By measuring the reciprocal space map at these angles, a component of the in-plane and out-of-plane lattice parameter can be measured. From both reciprocal lattice maps, we see that the in-plane component ( $q_x$ ) for the film roughly matches that of the substrate indicating fully coherent in-plane strain. The disproportionate weight of the film peak along the black line, and the lack of presence of any significant weight of the film peak along the gray line indicate that the films appear to be fully strained in the plane. This behavior is observed for all LCO films independent of oxygen pressures and film thickness up to 90nm for both STO and LSAT substrates. The pseudomorphic behavior is surprising given that we estimate the Matthews-Blakeslee critical thickness to be ~3.25nm on STO and ~7.25nm on LSAT.

The out of plane lattice parameters ( $a_c$ ) were measured as a function of oxygen deposition pressure and are plotted in Fig. 2.  $a_c$  is consistently lower for films grown on STO than on LSAT substrates as expected, since the STO places the LCO films under larger in-plane tensile strain compared to LSAT. The inset of Fig. 2. shows the single phase peaks of LCO in the  $\theta$ - $2\theta$  scans for films grown on STO in high and low oxygen deposition pressures.

Together the reciprocal space maps and  $\theta$ - $2\theta$  scans indicate that the in-plane lattice parameters remain more or less constant while the out-of-plane lattice parameters increase at lower oxygen deposition conditions. Assuming that the in-plane lattice parameters,  $a$  and  $b$ , are fixed to the lattice parameters of the surface unit cells of the substrates (3.87Å for LSAT and 3.905Å for STO) as indicated in the reciprocal lattice maps, we can conclude that the LCO unit cell volume increases as a function of decreasing oxygen deposition pressure which may be explained by the presence of oxygen vacancies at lower oxygen deposition pressures.<sup>14, 15</sup> Oxygen vacancies typically arise to preserve thermal equilibrium during the deposition process; the loss of the oxygen atom leaves extra electrons that may hop to nearby  $\text{Co}^{3+}$  forming larger  $\text{Co}^{2+}$  cations which in turn expand the lattice. The LCO/LSAT samples are slightly tetragonally distorted, while the LCO/STO samples exhibit a more severe tetragonal distortion that increases with higher oxygen deposition pressures. These tetragonal lattice distortions distinguish our LCO films from the bulk and may help to explain the ferromagnetism at higher oxygen pressures.

A comparison of XA and XMCD measurements of the Co  $L_{2,3}$  edges of our LCO thin films with multiplet calculations from Abbate *et al.* and bulk LCO spectra reveals that Co is in a 3+ valence state and suggests a high-spin configuration.<sup>8, 5, 16</sup> Fig. 3 shows a typical XMCD spectrum of LCO/STO samples grown in 200 mTorr and 10 mTorr of oxygen. The XMCD measurements indicate that the ferromagnetism from the  $\text{Co}^{3+}$  is suppressed for lower oxygen deposition conditions.<sup>8</sup>

In order to confirm that the ferromagnetism is a bulk effect, we have characterized the LCO thin films in a SQUID magnetometer. Fig. 4 shows both the temperature dependence of the magnetization as well as hysteresis loops of LCO/STO films grown in 10 mTorr and 320 mTorr of oxygen. A linear background in the high field range was subtracted from the data to account



for the diamagnetic contributions from the substrate. LCO samples of varying thickness deposited at 320 mTorr exhibited similar saturation magnetization values, thus suggesting that the observed ferromagnetism is not a surface or interface effect but a bulk effect. LCO/LSAT films grown at 320mTorr exhibit the highest saturation magnetization of approximately  $0.8\mu_B/\text{Co}$  with corresponding LCO/STO films of  $0.65\mu_B/\text{Co}$ . Assuming only a spin contribution to the magnetic moment from  $\text{Co}^{3+}$ , we expect a magnetic moment per Co to be  $0\mu_B$  (in a LS state),  $2\mu_B$  (IS) or  $4\mu_B$  (HS). The relatively low saturation magnetization values suggest that there is significant canting of the Co moments on the lattice. Alternatively, such low moment could be due to an inhomogeneous transition from the epitaxial strain of the Co atoms to higher spin states, implying the presence of a mixture of Co atoms in different spin states. Moreover, the maximum Curie temperature found for the high oxygen pressure LCO samples is  $\sim 80$  K with a suppression of the Curie temperature for lower oxygen pressures.

In perovskite oxides, the bonding of the transition metal to the octahedral oxygen cage lifts the degeneracy of the  $d$ -orbitals into  $e_g$  and  $t_{2g}$  levels and allows for different spin states. The bonding strength and amount of overlap between the bonding orbitals affect the relative crystal field splitting between the non-degenerate  $d$ -orbitals. The competition of crystal field energy with the Hund's exchange energy in a material system exhibiting critical spin behavior is crucial for understanding the spin state and the magnetic ordering. Structural and magnetic characterization of LCO films grown in varying oxygen atmospheres suggests that ferromagnetism is strongest when the films are more tetragonally distorted and the out-of-plane lattice parameters are smaller than in-plane lattice parameters, thus significantly altering the crystal field splitting. The suppression of ferromagnetism at lower oxygen deposition conditions

may be explained in terms of the larger out-of-plane lattice parameters and more cubic crystal structure.

In summary, we have synthesized ferromagnetic LCO thin films with varying oxygen pressure. The films grown on STO and LSAT substrates are tetragonally distorted as shown by XRD. We have shown that the ferromagnetic order found at low temperatures arises from the  $\text{Co}^{3+}$  ions and is suppressed by the decreased tetragonality possibly arising from oxygen vacancies. Correlation of the structural and magnetic properties suggests that the long range magnetic order is due to tetragonal distortions of the LCO structure.

This work was supported in full by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering as well as Scientific User Facilities Division of the U.S. Department of Energy under Contract Number: DE-AC02-05CH11231. We would like to thank Kin Man Yu at the Lawrence Berkeley National Laboratory Materials Science Division for RBS, James Rondinelli and Nicola Spaldin for their discussions. We would also like to thank Joanna Bettinger, Brittany Nelson-Cheeseman, Jodi Iwata, and Alex Grutter for discussions and support.

Captions:

FIG. 1 (color online) Reciprocal space maps at the (103) peak of LCO films on STO showing both in-plane and out-of-plane axes. Data obtained from films grown in (a) 20 mTorr and (b) 200 mTorr of oxygen both appear pseudomorphically strained to the substrate in the plane (horizontal axis).

FIG. 2 (color online) Dependence of the out-of-plane lattice parameter,  $a_c$ , on the oxygen pressure during deposition for films grown on STO (orange triangles) and LSAT substrates (blue circles). The pseudocubic bulk lattice parameter for LCO is  $3.80\text{\AA}$ . An increase in  $a_c$  with decreasing oxygen pressure is observed and films grown on LSAT have smaller  $a_c$  than those deposited on STO. Inset shows single phase behavior observed from  $\theta$ -2  $\theta$  scans of films grown in high(black) and low(orange) oxygen pressures on STO.

FIG. 3 (color online) (top) Co  $L_{3,2}$  XA spectra measured at 15K exhibiting slight differences in line shape between 10 mTorr (orange, open circles) and 200 mTorr (black, closed triangles) LCO films grown on Nb:STO. (bottom) XMCD difference signal showing increased dichroism from 200 mTorr sample at the  $\text{Co}^{3+}$  peak.

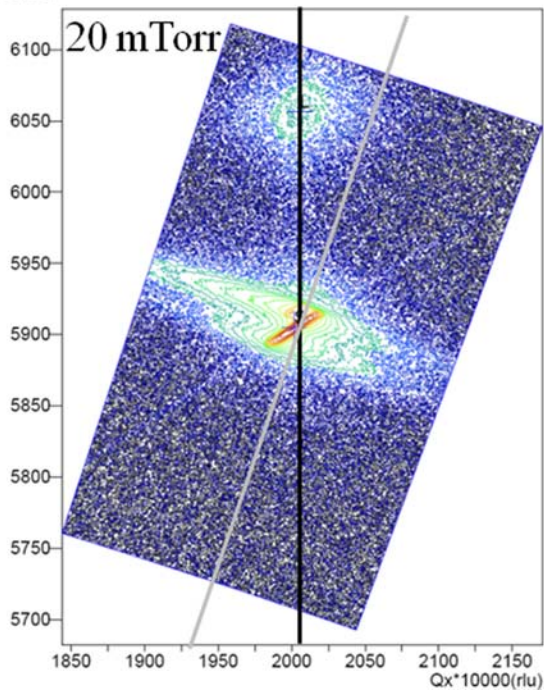
FIG. 4 (color online) Temperature dependence of the magnetization for LCO films grown in 10 mTorr (orange) and 320 mTorr (black) of oxygen on STO. The films were field cooled and then

measured in an applied field of 0.2 T. Inset shows magnetization versus applied field measurements taken at 5 K.

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