Strain-driven magnetism in LaCoO₃ thin films

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The electronic structure of epitaxial films on LaCoO₃ (LCO) has been studied within first-principles electronic structure calculations. A spin state transition is found to take place as a function of lattice strain which freezes in the intermediate spin state for nonzero strain. In contrast to earlier speculations this is found to arise from substrate strain alone and angle variations are small. The intermediate spin state also stabilizes ferromagnetism in the ground state. The anomalous temperature dependence of the x-ray absorption spectra for films of LCO on LCO and its absence in films of LCO on $(LaAlO_3)_{0.3}(SrAlTaO_6)_{0.7}$ is also explained.

$3d$ transition-metal oxides exhibit a wide range of electronic and magnetic properties as a result of coexisting spin, orbital, and lattice degrees of freedom, all of which requiring treatment at the same footing.[1] In recent times there has been a resurgence of interest in these materials with the specific aim of controlling their properties with external parameters such as strain, electric field, etc.[2] This is with the view of using them as new generation electronic components. A material that has been studied in this context is LaCoO₃ (LCO). Bulk LCO (Ref. 3) shows interesting temperature dependent properties and the aim has been to examine how one can modify the properties externally. Substrate strain[4] has been found to be a useful parameter to control the magnetism in the LCO overlayers. More recently LCO films have been grown on a piezoelectric substrate.[5] An electric field has been used to modify the substrate lattice constants and therefore the strain and consequent magnetism in the LCO overlayers. However the exact mechanism by which the magnetic state is altered is not very clear.

Bulk LaCoO₃ at low temperature is found to exhibit a low spin state with an electronic configuration of $t_{2g}^6 e_g^0$ on Co.[3,6] Susceptibility data[7] show a maximum at 90 K followed by a Curie-Weiss-type decrease at higher temperatures. This has been interpreted as arising from a spin state transition taking place as a function of temperature. The nature of the transition, however, is still very controversial with the debate[3,8,9] being whether it is a low spin to high spin transition or one to an intermediate spin state. This crossover takes place as a result of a delicate interplay between the crystal-field splitting and the intra-atomic exchange interaction. The temperature dependence is brought about by the dependence of the crystal-field splitting on the bond length[10] which in turn changes with temperature. This naturally suggests epitaxial strain as an alternate handle to tune the spin state transition and therefore change the magnetism.

Recently Fuchs *et al.*[4] have grown thin films of LCO on different substrates. Ferromagnetism has been found with a T_C (Curie temperature) of 85 K on $(LaAlO_3)_{0.3}(SrAlTaO_6)_{0.7}$ (LSAT) substrate, in addition to a strain dependent T_C. The origin of the ferromagnetism is however not clear, with a significant role played by the rotation of the CoO₆ octahedra being offered as one of the reasons.[4] To address this issue we have considered tetragonal unit cells of LCO where the in-

plane and out-of-plane lattice constants have been kept fixed to the experimental values.[4] We however allowed for a rotation of the CoO₆ octahedra which is a commonly observed lattice distortion in perovskite oxides[11] and optimized the total energy as a function of the angle. The paper by Fuchs *et al.*[4] speculated that the Co-O-Co angle strongly deviated from 180° for thin films grown on LaAlO₃ (LAO) and LCO substrates. However, the angles they speculated reached a value close to 180° in the films grown on LSAT and SrTiO₃ (STO). Thus the strong angle dependence of strain drove the spin state transition and hence gave rise to ferromagnetism. Contrary to their speculations we find that there is a very slight angle dependence of the strained films. This therefore cannot be the reason for the spin state transition observed by us in our calculations. We therefore conclude that it is the strain-induced pseudotetragonal structure which is responsible for the spin state transition. Further, as support to the model proposed by us, we are able to explain the temperature dependence of the x-ray absorption spectra within our calculations. Experimentally it was found that the films of LCO
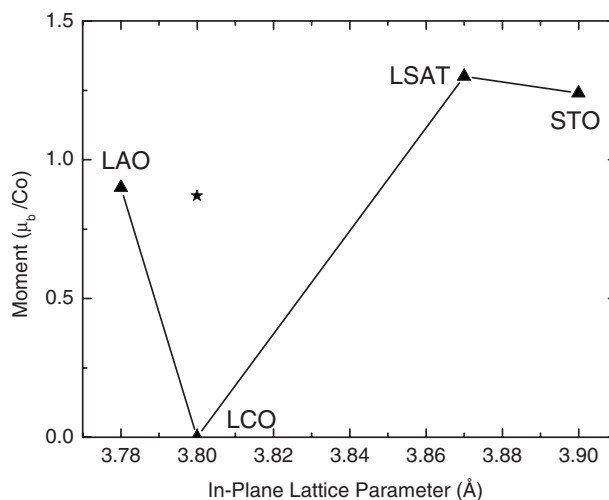

FIG. 1. The variation of the magnetic moment (triangles) on the Co site as a function of the in-plane lattice parameter for the ground state. The nature of the substrate has also been indicated. For LCO on LCO we also provide the moment of the ferromagnetic state (star) which lies close in energy to the nonmagnetic states.

TABLE I. Energies in eV for 4 f.u. of LCO grown on different substrates for different magnetic configurations.

	LCO/LCO	LCO/LAO	LCO/LSAT	LCO/STO
Nonmagnetic	−152.761	−152.742	−152.875	−152.793
A type	−152.746	−152.719	−152.827	−152.845
C type	−152.761	−152.736	−152.862	−152.793
Ferromagnetic	−152.742	−152.781	−152.953	−152.939

grown on LCO showed a strong temperature dependence of the O K edge as well as the Co L edge x-ray absorption spectra.[12] The L edge x-ray absorption spectra of the transition-metal atom are strongly sensitive to crystal field and spin state effects. Hence the temperature dependence has been compared to cluster calculations for CoO_6 clusters and interpreted as arising from spin state transitions. LCO films grown on LSAT substrate however did not show any significant temperature dependence. Comparing the total energies obtained by us from calculations for different magnetic states, we find that for LCO on LCO the nonmagnetic solution as well as the other magnetic solutions lies very close in energy. The magnetic solutions correspond to an intermediate spin state. We show that temperature effects change the relative concentrations of low spin and intermediate spin states, hence explaining the temperature dependence of the spectra. However as the substrate strain is varied, the intermediate spin state gets frozen in as the ground state; the low spin state lies much higher in energy and hence there is no temperature dependence.

We have performed *ab initio* calculations for the electronic structure of thin films of LCO using a plane-wave pseudopotential implementation of density-functional theory as implemented in VASP.[13] Projector-augmented wave potentials[14] have been used, in addition to the generalized gradient approximation to the exchange part of the functional. A tetragonal unit cell was considered by us where the lattice constants were fixed at the experimental values.[4] The effect of the substrate was included by fixing the in-plane lattice constant to that of the substrate. We also included a $GdFeO_3$ type rotation of the octahedra which is normally observed in perovskite oxides[11] and the total energy was minimized as a function of the angle. A k point mesh of $4 \times 4 \times 4$ was considered for the total-energy calculations but increased to $8 \times 8 \times 8$ for the density of states calculations using the tetrahedron method. Spheres of radii 1.3, 1.2, and

1.2 Å were considered on La, Co, and O for evaluating the magnetic moment and the orbital-projected density of states.

In Fig. 1 we have plotted the variation of the magnetic moment on the Co site as a function of the in-plane lattice parameter. For LCO films on LCO we show both the nonmagnetic moment as well as the moment for the structure exhibiting the ferromagnetic state. The dependence on the in-plane lattice constant is nonmonotonic. It should be noted that LCO exhibits a pseudotetragonal unit cell for all values of the substrate lattice constant except for LCO on LCO where it is pseudocubic. Further LCO on LAO represents compressive strain while LCO on LSAT and STO represents tensile strain. Examining the total energies given in Table I, we find that the ferromagnetic state is the ground state in every case except for LCO on LCO where all magnetic states as well as the nonmagnetic state lie very close to each other in energy.

The Co-O-Co angle variations for the ground-state structure as a function of the in-plane and out-of-plane lattice constants are given in Table II. Earlier reports suggest that a change in the angle drives the spin state transition. The in-plane angle changes are small and cannot explain the stabilization of the ferromagnetic state for finite strain. The out-of-plane Co-O-Co angles are found to decrease with the strain in contrast to earlier speculations where angles were expected to approach 180° for films of LCO on LSAT/STO. Hence it is primarily the change in bond lengths as a result of substrate strain which drives the system into the ferromagnetic state.

The question we asked next was what was the spin state stabilized in the ferromagnetic state. To address this we have plotted the Co d projected up- and down-spin partial density of states for t_{2g} and e_g symmetries in Fig. 2 for LCO on LSAT. In the tetragonal case there is a further splitting of the t_{2g} orbitals into doubly degenerate d_{xz} and d_{yz} as well as singly degenerate d_{xy} orbitals. Similarly there is a splitting of the e_g orbitals into singly degenerate $d_{x^2-y^2}$ and $d_{z^2-y^2}$ orbitals. However these splittings are small and so we choose to still discuss the electronic structure in terms of the nomenclature valid for the cubic case. From the density of states [Fig. 2(a)] we find that the up-spin t_{2g} states are fully occupied while the down-spin t_{2g} states are partially occupied. In addition the up-spin e_g states are partially occupied [Fig. 2(b)]. For a high spin configuration we would have the t_{2g} and e_g up-spin states fully occupied before the t_{2g} down-spin states are filled. Hence an intermediate spin state $(t_{2g\uparrow}^3 t_{2g\downarrow}^2 e_{g\uparrow}^1)$ is stabilized on Co for LCO on LSAT. This is seen to be the

TABLE II. Co-O-Co angle in x, y, and z directions for LCO grown on different substrates. In-plane and out-of-plane lattice constants are also given.

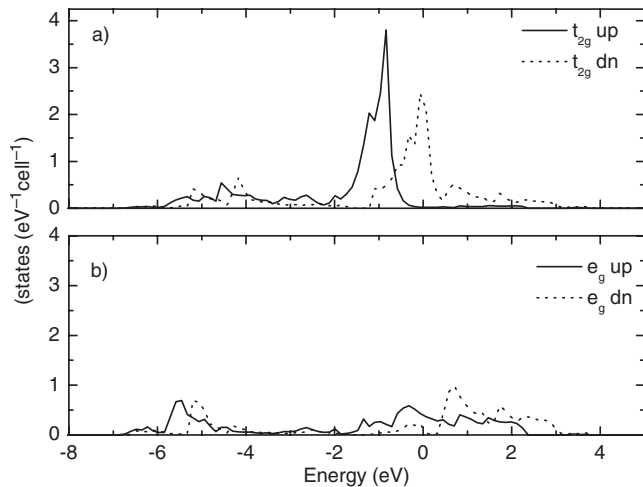| Substrate	Lattice constant		Co-O-Co angle		
	In plane	Out of plane	x direction	y direction	z direction
LAO	3.78	3.87	163.3	163.3	160.9
LCO	3.8	3.8	162.2	162.2	158.3
LSAT	3.87	3.8	163.2	163.2	157.6
STO	3.9	3.79	163.1	163.1	156.7

FIG. 2. Co d projected up- and down-spin partial densities of states for t_{2g} and e_g symmetries for LCO on LSAT.

FIG. 3. Co d projected partial density of states for (a) ferromagnetic case and (b) nonmagnetic case for films of LCO grown on LCO.

case even for LCO on LCO for the ferromagnetic case [Fig. 3(a)]. The partial occupancy of the t_{2g} down-spin levels as well as the e_g up-spin levels favors a ferromagnetic state as the ground state for LCO on LSAT and STO.

Recent x-ray absorption experiments[12] carried out at the Co $L_{2,3}$ edge for the epitaxial films showed a strong temperature dependence for LCO on LCO. This was absent for LCO films grown on LSAT. They interpreted the results in terms of a spin state transition taking place as a function of temperature for LCO on LCO films. Our total-energy calculations for magnetic and nonmagnetic solutions indicate that the solutions lie very close in energy for LCO on LCO while the difference is large in all other cases considered by us. The effect of temperature is simulated by us by considering pseudocubic unit cells with a uniform expansion of the unit-cell volume. We have computed the total energies for different magnetic configurations and we find that for an expansion of 1% of the lattice constant, the ferromagnetic state gets stabilized by 60 meV. Thus as a function of temperature the relative weight of intermediate and low spin state in the ground-state wave-function changes, giving rise to the temperature dependence. Plotting the Co d projected partial density of states for LCO on LCO considering the nonmagnetic and ferromagnetic solutions we find that the densities of states are very different in the two cases (Fig. 3). The nonmagnetic solution [Fig. 3(a)] has the low spin stabilized, while the ferromagnetic solution [Fig. 3(b)] has the intermediate spin stabilized. The partial densities of states are consequently different in the two cases. Although multiplets are important in the description of the x-ray absorption spectra at the $L_{2,3}$ edge, these results indicate that the final states are different and can therefore explain the temperature dependence seen in experiment.

It is for this reason that we choose to explain the O K edge x-ray absorption spectra where initial-state core hole effects as well as multiplet effects are not important. The experimental spectrum corresponds to transitions from the oxygen $1s$ level to the unoccupied oxygen states with $2p$ character. Hence the experimental spectrum may be compared to the broadened O p partial density of states, with the
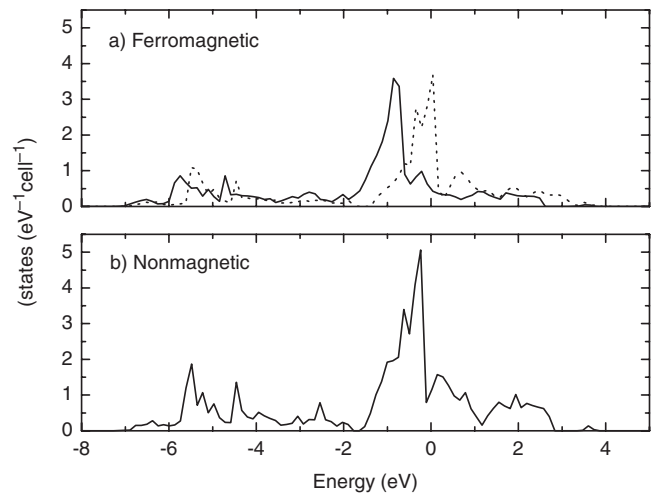
broadening accounting for instrumental resolution among other effects. The results of such a comparison are shown in Fig. 4 considering the calculated O p densities of states for the ferromagnetic case as well as the nonmagnetic case. There is transfer of spectral weight in the low energy region from the nonmagnetic to the ferromagnetic spectral function. A similar transfer of spectral weight is seen in the high energy region around 3.0–4.0 eV. This could explain the trend seen in experiments for LCO on LCO as a function of temperature.

In the results discussed until now we have analyzed the results from bulk calculations for LaCoO₃ where the effect of the substrate is taken in defining the in-plane lattice constants. The electronic and magnetic structures could strongly deviate at the interface as well as at the surface. In order to analyze this we have considered films of LaCoO₃ grown on STO substrate consisting of 16 layers of LCO grown in a symmetric slab arrangement on STO. At the surface as well as at the interface we find a significant reduction in the moment from bulklike values. However no significant moment or occupancy of the Ti layers is found.
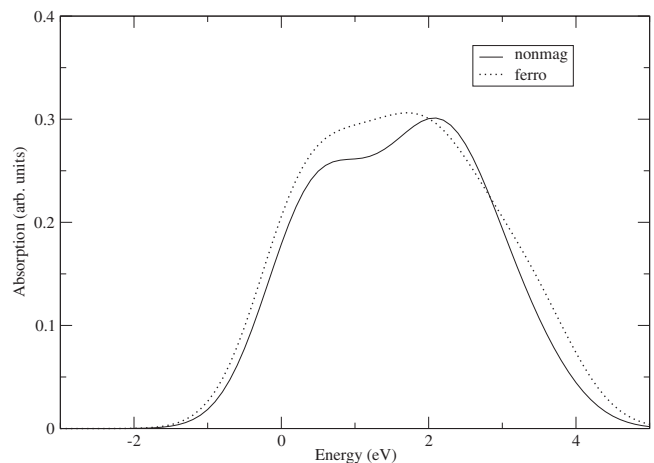

FIG. 4. Calculated O K edge x-ray absorption spectra for nonmagnetic (solid line) as well as ferromagnetic cases (dashed line).

We have carried out *ab initio* electronic structure calculations for epitaxial films of $LaCoO_3$ grown on various substrates. We find that the intermediate spin is frozen in for the cases in which a pseudotetragonal structure is stabilized and the films are subject to compressive or tensile strain. The stabilization of the intermediate spin state also makes the ferromagnetic state to have lowest energy. LCO on LCO is found to have a pseudocubic structure. Total-energy calculations reveal that the nonmagnetic and magnetic solutions lie close in energy for the ground-state lattice constant with the energy difference changing for a uniformly expanded or contracted case, thus explaining the temperature dependence observed in x-ray absorption spectra.

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