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Reversible strain effect on the magnetization of $LaCoO_3$ films

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The magnetization (M) of a $LaCoO_3$ film grown epitaxially on a piezoelectric substrate has been investigated in dependence on the biaxial in-plane strain. M decreases with the reversible release of tensile strain, with a maximum change of at least 6% per 0.1% of biaxial strain near the Curie temperature (T_C). The biaxial strain response of T_C is estimated to be below 5 K/% in the tensile strain state. This is in agreement with results from statically strained films on various substrates. As possible origins of the strain-induced magnetization are considered (i) the strain-dependent Curie temperature, (ii) a strain-dependent magnetically inhomogeneous (phase-separated) state, and (iii) a strain-dependent magnetic moment (spin state) of Co ions. The T_C shift is found insufficient to explain the measured strain-induced magnetization change but contributions from mechanism (ii) or (iii) must be involved.

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The perovskite-type $LaCoO_3$ (LCO) has been intensively studied, mainly because of the thermally driven spin state transitions of Co^{3+} ions, which give rise to unique properties.[1–3] Despite large experimental and theoretical efforts,[4–12] the spin state of $LaCoO_3$ at finite temperatures remains controversial. The ground state of $LaCoO_3$ is nonmagnetic with Co^{3+} ions in the low-spin (LS) ($S=0$) state.[1] At temperatures above 100 K, Co^{3+} ions display various spin states due to a delicate balance between the crystal-field splitting Δ_{CF} and the intra-atomic Hund exchange.[1,3] Since Δ_{CF} is very sensitive to the variation in the Co-O bond length,[13] structural distortions may modify the Co spin state. Recently, $LaCoO_3$ has attracted renewed interest due to the observation of ferromagnetism in epitaxially strained thin films.[14,15] Actually, the existence of either long- or short-range ferromagnetic order has been reported for various types of $LaCoO_3$ samples,[14–21] among them also nanoparticles.[16,21]

The origin and nature of the observed ferromagnetism are currently under investigation. In ferromagnetic strained films and nanoparticles, Co ions are in an excited spin state at $T=0$, and ferromagnetic exchange interactions are present. The magnetic state might be phase separated into ferromagnetic and nonmagnetic clusters, as has been reported for lightly doped $La_{1-x}Sr_xCoO_3$.[22] Which key parameter(s) change(s) between the nonmagnetic ground state of crystals and this ferromagnetic state? If one assumes unchanged composition (no unintended doping), structural changes in Co-O bond lengths and bond angles should be involved, as discussed in the work on thin films[15] and nanoparticles.[16,21] For nanoparticles, an enhancement of the volume of the unit cell has been proposed as a key parameter for the appearance of ferromagnetism,[16,21] related to the larger radius of Co ions in excited spin states. The effect of biaxial tensile strain in films includes both an enhanced unit-cell volume ($V=a^2c$) and a tetragonal distortion c/a, with the film's pseudotetragonal in-plane (out-of-plane) lattice parameter a (c). $LaCoO_3$ is rhombohedral in bulk[23] but the pseudotetragonal description of strained films is assumed to be a useful approximation.

Thin films grown epitaxially on piezoelectric single-crystalline substrates of $Pb(Mg_{1/3}Nb_{2/3})_{0.72}Ti_{0.28}O_3(001)$ (PMN-PT) allow direct investigations of strain-dependent properties.[24–26] The strain of the films can be reversibly and uniformly controlled by the inverse piezoelectric effect of the substrate. The poled PMN-PT(001) crystals used as substrates are monoclinic with very tiny distortions with regard to the cubic structure.[27] Thus, the influence of the biaxial strain on the magnetization of a film can be measured directly and quantitatively, independent of the effects of other parameters, e.g., oxygen nonstoichiometry, chemical inhomogeneities, and microstructure.

We report on the influence of reversible strain on the magnetization of $LaCoO_3$ films epitaxially grown on PMN-PT(001). A reversible roughly linear decrease in the magnetization with the piezoelectrically controlled release of tensile strain is observed at various temperatures below the Curie temperature (T_C), giving direct evidence for a strain effect. In order to draw conclusions from the data, the following mechanisms for the strain-dependent magnetization have been considered: (i) the strain-dependent T_C, (ii) a strain-dependent magnetically inhomogeneous (phase-separated) state, and (iii) a strain-dependent magnetic moment (spin state) of Co ions. Regarding (i), an upper limit for the strain response of T_C is estimated. The T_C shift by strain is found insufficient to explain the measured strain-induced magnetization in the temperature range of 30–70 K, and contributions from mechanism (ii) or (iii) must be involved.

Epitaxial LCO films have been grown on various substrates [$SrTiO_3$ (STO), $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.35}$ (LSAT), $LaAlO_3$ (LAO), and PMN-PT, all in (001) orientation] by pulsed laser deposition (KrF 248 nm) from a stoichiometric target. The deposition temperature and the oxygen background pressure were 650 °C and 0.45 mbar, respectively. After deposition, the films were annealed for 10 min at the deposition pressure and cooled down in oxygen atmosphere of 800 mbar. Structure and film thickness were characterized by x-ray diffraction (XRD) measurements with a Philips X'Pert MRD diffractometer using Cu K_α radiation. The magnetization (M) was measured in a superconducting quantum interference device magnetometer. T_C is estimated with a precision of about 1 K by extrapolating M^2 for temperatures $T<T_C$ to $M=0$. For the film grown on $LaAlO_3$, T_C is estimated as the highest temperature where a distinct remanent magnetization was observed. During strain-dependent mea-

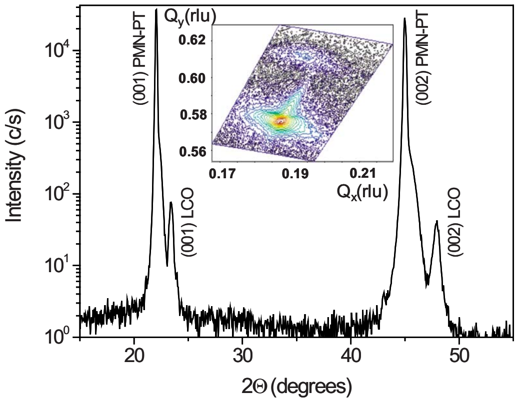

FIG. 1. (Color online) $\Theta-2\Theta$ XRD of a 50-nm-thick LCO/PMN-PT(001) film. Inset: XRD reciprocal space map around the (013) reflection.

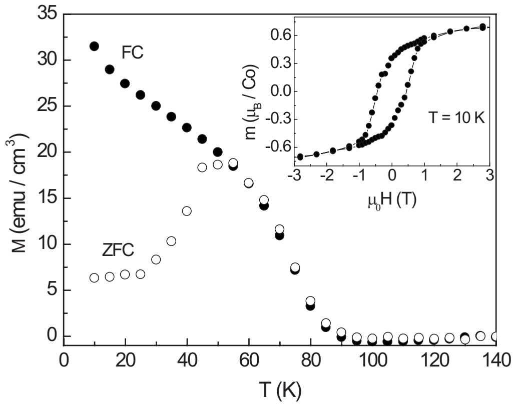

FIG. 2. Temperature-dependent in-plane magnetization of a 50 nm LCO film measured both in field-cooled and zero-field-cooled modes in a field of 200 mT along the [100] substrate direction. Inset: magnetic hysteresis loop at 10 K.

surements, an electrical voltage ≤400 V is supplied to the substrate between the magnetic film and a bottom electrode on the opposite (001) surface of the substrate. The current in this circuit is below 100 nA for constant voltage and temperature.

The XRD scans of a 50-nm-thick film on PMN-PT which is used for the reversible strain studies are given in Fig. 1. PMN-PT and bulk LCO have pseudocubic lattice parameters of 4.02 (Ref. 24) and 3.805 Å,[23] respectively. Despite the large misfit of 5.7%, LCO grows epitaxially oriented on PMN-PT(001). X-ray reciprocal space mapping around the (013) asymmetric reflection reveals partial relaxation of the LCO film (inset of Fig. 1). The lattice parameters are $c=3.79$ Å and $a=3.88$ Å. The tetragonal distortion is estimated as $t=c/a=0.977$, revealing substantial residual tensile strain of the film. The pseudotetragonal lattice parameters a and c obtained from X-ray $\Theta-2\Theta$ scans and reciprocal space maps for 100-nm-thick films on various substrates are listed in Table I. We note that the 50- and 100-nm-thick films on PMN-PT are quite similar, as can be seen from their value of T_C below and their lattice parameters. The thinner film has been chosen for the reversible strain study originally to ensure its complete straining by the substrate. The composition of the films has not been investigated in detail, in particular there may be slight deviations in the oxygen or metal cation content from the nominal ones.[12] However, the ferromagnetic Curie temperatures of the tensily strained films prove to be comparable with those reported by Fuchs *et al.*[15] for the same respective in-plane parameter and similar thickness.

All epitaxial films are found to be ferromagnetic in the sense that a significant remanent magnetization is present at low temperature (10 K) and $M(T)$ curves show a distinct onset of magnetization. The film on $LaAlO_3$ is an exception concerning the second statement; the onset of M is not well defined which may be the reason for the different values of T_C reported in earlier work.[15] In Fig. 2 we plot M vs T of the 50 nm film on PMN-PT measured in field-cooled (FC) and zero-field-cooled (ZFC) modes in a magnetic field of $\mu_0 H=200$ mT applied along the [100] in-plane direction. T_C has been determined as 85 K, a value that fits nicely the data of T_C vs a reported by Fuchs *et al.*[15] The inset shows $M(H)$ at 10 K. M takes a value of $0.65\mu_B$/Co under 3 T and is not saturated, indicating the absence of a homogeneous collinear ferromagnetic state. One possible explanation is a frozen cluster state as discussed for low-doped cobaltites.[28] A cusp in the ZFC magnetization is found at ~50 K, which may indicate a freezing temperature of clusters. The coercive field at 10 K is 450 mT, a rather high value that may reflect strong magnetocrystalline anisotropy contributions. Both the values of quasisaturated magnetization and coercivity are in reasonable agreement with the available published data[14,15] but more work is needed to understand the detailed magnetic nature of strained $LaCoO_3$ films.

In the following we describe the results of reversible biaxial strain measurements on the magnetization of LCO at constant temperature and magnetic field. This mode of measurement proved to be the most precise since the strain effect on M is small against the background noise. M vs strain in the reversible regime of 0.1% strain turned out to be linear

TABLE I. In-plane (a) and out-of-plane (c) lattice parameters, unit-cell volume ($V=a^2c$), and T_C of LCO films grown on various substrates. a_{sub} is the pseudocubic substrate lattice parameter. The unit-cell volume of bulk LCO is 55.08 Å^3.

LCO films (100 nm)	a_{sub} (Å)	c (Å)	a (Å)	V (Å^3)	T_C (K)
LCO/LSAT	3.87	3.804	3.867	56.88	85
LCO/STO	3.905	3.785	3.896	57.45	86
LCO/PMN-PT	4.02	3.81	3.87	57.06	87
LCO/LAO	3.79	3.85	3.789	55.27	75

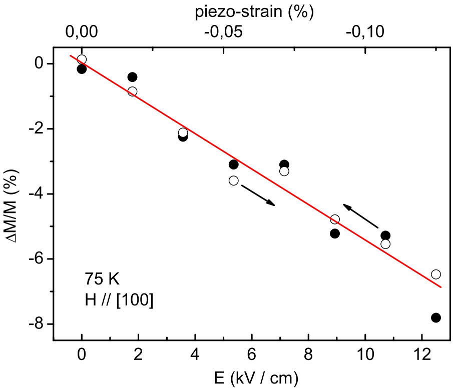

FIG. 3. (Color online) Strain-dependent change in the magnetization $[M(E)-M(0)]/M(0)$ recorded at $T=75$ K in FC mode at 200 mT, with the electric field (E) applied to the substrate. The tensile strain of the as-grown film is released proportional to E. The line indicates the best linear fit to the data.

and has been fitted accordingly. We note that the alternative recording of $M(H)$ loops in different strain states is less accurate for the present case since the $M(H)$ curve cannot be readily fit to eliminate the noise. Magnetization vs strain data at constant temperature have been collected in the FC state at 200 mT, a condition that provides a nearly saturated state in the sense that, even though the film cannot be fully saturated, its ferromagnetic domains have been aligned. Data have been measured from 30 to 85 K, an example is given in Fig. 3. The E-field-controlled contraction of the substrate of $\sim 0.1\%$ for $E=10$ kV/cm induces a decrease in M. Since the film is under tensile strain, the contraction means a slight release of the as-grown strain. Hence, one concludes that M increases with tensile strain in the LCO film which is an observation opposite to both the results for a doped $La_{0.7}Sr_{0.3}CoO_3$ film[25] and the behavior of double-exchange-dominated ferromagnetic manganites.[24] The temperature dependence of the such determined strain response $\Delta M/M$ of the magnetization can be seen in Fig. 4. $\Delta M/M$ takes a maximum near T_C and decreases gradually toward lower temperature until it reaches a value of about 1% at 30 K. Due to the experimental setup (probably because of electrical break down through the He atmosphere in the cryostat), the strain response could not be measured below this temperature. At this point we need to comment on the possible influence of a temperature-dependent piezoelectric strain from the substrate. As it appears there are no published strain data for PMN-PT for the low-temperature range available. An x-ray study of lattice parameters indicated little reduction in the piezostrain between 300 and 90 K.[27] Furthermore, transport measurements vs strain conducted at 30 K (Ref. 29) worked well. Thus, we assume for the present experiment that, despite of a possible reduction in the strain from 85 to 30 K, the drop of $\Delta M/M$ is essentially an inherent property of the LCO film, and not a result of the reduced piezoelectric substrate strain.

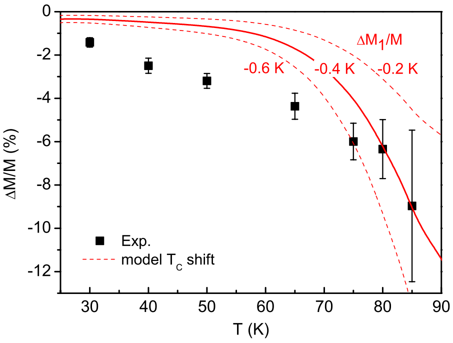

FIG. 4. (Color online) Temperature dependence of the strain-induced M change (conditions as in Fig. 3) between $E=0$ and 10 kV/cm. The lines denote the estimated M change for a given strain-induced shift of T_C (see text).

The observed increase in M with tensile strain confirms the observation of Fuchs and co-workers[14,15] that tensile strain stabilizes ferromagnetism in $LaCoO_3$ films. As to the origin of the strain-dependent M, we first consider and estimate the strain-dependent shift of the magnetic ordering temperature. From the sign of M change, it is obvious that T_C would increase with tensile strain, as is consistent with the T_C vs in-plane parameter data reported by Fuchs *et al.* (Fig. 6 in Ref. 15). On the other hand, those data as well as our data in Table I for films on various substrates indicate that dT_C/da may not be large but amounts to few kelvin per 1% of strain. One may think of directly recording $M(T)$ in different reversible strain states. However, the smallness of the reversible strain and the error of the T_C extrapolation procedure render this approach unreliable. Instead, the T_C shift induced by the reversible strain is estimated from strain-dependent M data as follows. The M change ΔM_{T_C} resulting from a T_C shift can be approximated by shifting the $M(T)$ curve (recorded under equal conditions as the M vs strain data) by an assumed temperature interval ΔT_C and taking the difference to the original data. The thus obtained value, denoted as ΔM_1, overestimates ΔM_{T_C} at lower T and converges to the real value close to T_C. Figure 4 shows the $\Delta M_1(T)$ curve calculated for several values of ΔT_C such as -0.2, -0.4, and -0.6 K. The value of ΔT_C is chosen to fit the data close to T_C (see Fig. 4) although one needs also to take into account that absolute M data get less precise with higher temperature. Here, we conclude a value of ΔT_C of ≤ 0.5 K since the measured value (plus error bar) may not be smaller than the model value. The derived ΔT_C provides an upper limit for the real T_C shift caused by the reversible strain of 0.1% in the LCO film. Hence, for the as-grown state of $a = 3.88$ Å of the LCO film, the biaxial strain dependence of the Curie temperature is estimated as $dT_C/da \leq 5$ K/%.

The thus estimated strain dependence of the Curie temperature does not explain the strain-induced M change in the range of 30–70 K since the latter substantially exceeds the $\Delta M_1(T)$ limit in Fig. 4. Hence, further mechanisms driven by the strain must contribute to the observed effect. Since LCO films may be in an inhomogeneous magnetic cluster state, strain may affect the clusters, increasing the ferromagnetic volume fraction or the magnetic moment of both the clusters and the matrix phase. The increase in the ionic magnetic moment of Co ions in the sense of a spin state change driven by tensile strain is also consistent with our data. These two mechanisms cannot be distinguished based on the present experiment but other methods exploring the local state of LCO films are needed to clarify this crucial point.

Finally, it seems interesting to consider the roles played by the tetragonal distortion and the volume change in the unit cell both induced by the epitaxial strain. Tensile strain tends to increase the volume; thus, its effect is opposite to hydrostatic pressure. Co ions in $LaCoO_3$ have been reported to transfer to the low-spin state under hydrostatic pressure,[30] as is also observed for the doped $La_{0.82}Sr_{0.18}CoO_3$.[31] This is consistent with the enlarged ionic radius of Co ions in the excited, i.e., intermediate or high spin states.[23] Hence, the idea has been expressed repeatedly that a volume increase is likely to stabilize excited spin states of Co ions. Fita *et al.*[21] and Zhou *et al.*[16] discussed this idea for the ferromagnetism observed in nanoparticles, the first reference providing structural data on bond lengths, angles, and unit-cell volumes of the nanoparticles. Our films (both under tensile and compressive in-plane strains) show an enhanced volume (Table I) with respect to the bulk unit cell of $LaCoO_3$. Thus, it is not unlikely that a volume increase in the LCO unit cell stabilizes an excited spin state of Co ions, as a necessary prerequisite for ferromagnetism. The effect of the tetragonal distortion, on the other hand, is less clear by now. A T_C of about 85 K has been reported also for samples virtually free from tetragonal distortion; examples are the nanoparticles[16,21] and the $LCO/SrLaAlO_4$ film discussed in Ref. 15.

Summarizing, the influence of reversible biaxial strain on the magnetization of ferromagnetic $LaCoO_3$ films under epitaxial tensile strain has been investigated. The change in magnetization with 0.1% of reversible strain is moderate (few percent) at all temperatures below T_C. The strain-induced increase in T_C is estimated to be below 5 K/% of strain (for a film with an in-plane parameter of $a=3.88$ Å) which is a rather small value but remarkable for the unusual enhancement of T_C by tensile strain. The T_C shift alone is found insufficient to explain the measured strain-induced magnetization between 30 and 70 K. Our results suggest an enhanced ionic magnetic moment of Co ions or a strain effect on a magnetically phase-separated state. Soft x-ray absorption experiments, which may give more insight into the effect of strain on the electronic structure, are in progress.

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