Reversible strain effect on the magnetization of LaCoO$_3$ films

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(Dated: May 7, 2008)

The magnetization of ferromagnetic LaCoO$_3$ films grown epitaxially on piezoelectric substrates has been found to systematically decrease with the reduction of tensile strain. The magnetization change induced by the reversible strain variation reveals an increase of the Co magnetic moment with tensile strain. The biaxial strain dependence of the Curie temperature is estimated to be below 4 K/% in the as-grown tensile strain state of our films. This is in agreement with results from statically strained films on various substrates.

PACS numbers: 75.70. Ak, 71.27.+a, 75.80.+q

Keywords: LaCoO$_3$, thin films, ferromagnetism

The perovskite-type LaCoO$_3$ has been intensively studied, mainly because of the thermally driven spin state transitions of Co$^{3+}$ ions, which give rise to unique properties.

Despite large experimental and theoretical efforts, 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. At temperatures above 100 K, Co$^{3+}$ ions display various spin states due to a delicate balance between the crystal-field splitting $\Delta_{\text{CF}}$ and the intraatomic Hund exchange. Since $\Delta_{\text{CF}}$ is very sensitive to the variation of the Co-O bond length, structural changes may easily modify the Co spin state. Recently, LaCoO$_3$ has attracted renewed interest due to the observation of ferromagnetism in epitaxially strained thin films. Actually, the existence of either long- or short-range ferromagnetic order has been reported for various types of LaCoO$_3$ samples. The origin of the observed ferromagnetism is currently under investigation.

Thin films of complex magnetic oxides grown epitaxially on piezoelectric single-crystalline substrates of Pb(Mg$_{1/3}$Nb$_{2/3}$)$_{0.72}$Ta$_{0.28}$O$_3$(001) (PMN-PT) allow direct investigations of their strain-dependent magnetism. The as-grown strain state of the films can be dynamically tuned by the inverse piezoelectric effect of the substrate, thus providing an opportunity to record the change with respect to strain of the ordering temperature or the magnetization for the particular as-grown strain state. Thus, the influence of strain on magnetism can be clearly separated from 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 thin LaCoO$_3$ films epitaxially grown on PMN-PT(001). A roughly linear decrease of the magnetization with the piezoelectrically controlled release of tensile strain is observed at various temperatures below the Curie temperature ($T_C$). From the measured reversible magnetization change, an upper limit for the strain-dependent shift of $T_C$ is estimated. Strain-dependent magnetization data give evidence for an enhanced magnetic moment of Co ions under tensile strain.

LaCoO$_3$ (LCO) films of various thicknesses were grown on PMN-PT(001) by pulsed laser deposition (KrF 248 nm) from a stoichiometric target. The deposition temperature ($T$) and the oxygen background pressure were 650°C and 0.45 mbar, respectively. After deposition, the films were annealed for 10 minutes 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 Kα radiation. The magnetization ($M$) was measured in a SQUID magnetometer. $T_C$ is estimated by extrapolating $M^2$ for $T < T_C$ to $M = 0$. For strain-dependent measurements, an electrical voltage is supplied to the substrate between the magnetic film and a bottom electrode on the opposite (001) surface of the substrate. The current in the piezo-circuit is below $10^{-6}$ A.

X-ray Θ–2Θ scans show clear (00l) film reflections characteristic of a pseudocubic structure (Fig. 1). PMN-PT has a pseudocubic lattice parameter of 4.02 Å and weak rhombohedral or monoclinic distortions. Bulk LCO is rhombohedral with a pseudocubic lattice parameter of 3.805 Å. Despite the large misfit of 5.7 %, LCO grows epitaxially oriented on PMN-PT(001). In-plane X-ray reciprocal space mapping around the (013) asymmetric reflection reveals partial relaxation of the LCO film, i.e. the reflections of the film and the substrate have different $Q_0$ values (Fig. 1 inset). The derived out-of-plane (c) and in-plane (a) lattice parameters are $c = 3.79$ Å and $a = 3.88$ Å for the 50 nm thick film. The tetragonal distortion estimated as $t = c/a$ is 0.977.

In Fig. 2 we plot $M$ vs $T$ of the film from Fig. 1 measured in field-cooled (FC) and zero-field-cooled (ZFC) modes in a magnetic field ($H$) of $\mu_0 H = 200$ mT applied along the in-plane [100] direction. Magnetic ordering is observed below about 87 K. A cusp in the ZFC magnetization is found at $\sim 50$ K, possibly indicating a glass-like behaviour as in bulk cobaltites. The inset shows the magnetization loop ($M(H)$) at 10 K. Clearly, the LCO film is ferromagnetic at low temperatures, with $T_C \approx 87$ K. This value agrees well with recently published data for strained LCO films. The coercive field ($H_c$) at 10 K is 450 mT.

In the following we discuss the effect of reversible bi-
 axial strain on the magnetization of LCO. Fig. 3a shows the $M$ dependence on the applied substrate electric field ($E$) at 75 K, recorded in 200 mT after field cooling. The increasing electric field leads to linear in-plane compression of the substrate and, hence, to reduction of the tensile film strain. The value of the piezoelectrical substrate strain at 10 kV/cm is about $-0.1\%$ at 90 K. A roughly linear, low-hysteresis decrease of $M$ is observed with increasing $E$, i.e. with decreasing tensile strain. A similar behaviour occurs at various temperatures; the resulting $M$ change measured at $E = 10$ kV/cm is summarized in Fig. 3b. A $M$ change of $\approx 9\%$ is observed near $T_C$. In order to clarify the strain effect also for the saturated magnetization, full $M(H)$ loops ($H < 5$ T) were recorded at 70 K in different strain states. They revealed a similar strain-induced change of the saturated magnetization; see, e.g., the data point for 70 K inserted in Fig. 3b.

The observed decrease of $M$ with reduced tensile strain confirms the observation of Fuchs et al.\textsuperscript{12,13} that tensile film strain stabilizes ferromagnetism in LaCoO$_3$. This may involve strain-induced enhancements of (i) the magnetic moment of the Co ions and (ii) $T_C$ with tensile strain. In the following we attempt to separate both effects.

As a first step, the $T_C$ shift induced by the reversible strain is estimated. The $M$ change $\Delta M_{T_C}$ resulting from a $T_C$ shift can be approximated by shifting the $M(T)$ curve (recorded under equal conditions as for the reversible strain runs) by an assumed temperature interval $\Delta T_C$ and taking the difference to the original data. The thus obtained $M$ change, denoted as $\Delta M_1(T)$, overestimates $\Delta M_{T_C}$ at lower $T$ and converges to its real value close to $T_C$. Fig. 3b shows the $\Delta M_1(T)$ curve calculated for $\Delta T_C = 0.4$ K. This value of $\Delta T_C$ is chosen to fit the measured $\Delta M$ at 80 K, close to $T_C$. Therefore, it 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 change of the transition temperature is estimated

| LSCO films   | $a_{sub}$ (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        |
| LSCO/LAO     | 3.79          | 3.85    | 3.789   | 55.27      | 75        |
as \( \Delta T_C/\Delta a \leq 4 \text{ K}/\% \).

As a consequence of the above arguments, the measured strain-induced \( M \) change in the range of \( T = 30 \pm 70 \text{ K} \) cannot originate from a \( T_C \) shift alone, since it substantially exceeds \( \Delta M_1(T) \) giving an upper limit to the \( M \) change caused by the \( T_C \) shift. Clearly, a decrease of the Co magnetic moment itself is needed to explain the data.

The above estimated maximum shift of \( T_C \) of 4 K/\% of biaxial strain for the as-grown state of \( a(LCO) = 3.88 \text{ Å} \) can be compared to the Curie temperature vs strain for LCO films grown on various substrates, see Tab. 1 and Ref. 12. We find little variation of \( T_C \) in the range of 2 K for \( a = 3.867 \pm 3.896 \text{ Å} \), indicating a weaker than the estimated maximum strain response of \( T_C \). It is worth noting that a compressively strained LCO film \( (a = 3.789 \text{ Å}) \) grown on LaAlO\(_3\) shows a remanent magnetization up to 75 K, too. Hence, the strain effect on \( T_C \) appears to be rather moderate.

Finally, it is interesting to consider the roles played by (i) the tetragonal distortion of the film characterized by the \( c/a \) ratio and (ii) the strain-induced volume \( (V) \) change of the unit cell. Tensile strain typically increases \( V \). 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\( 22 \), as is also found for the doped \( \text{La}_{0.82}\text{Sr}_{0.18}\text{CoO}_3\). This is consistent with the enlarged ionic radius of Co ions in the excited, i.e. intermediate/high, spin states\( 23 \). Hence, a \( V \) increase is likely to stabilize excited spin states of Co ions. Zhou et al.\( 14 \) indicated that volume increase may underlie the ferromagnetism observed in the LCO nanoparticles investigated in their work. The tetragonal distortion, on the other hand, seems to be less important for establishing ferromagnetism in LCO\(_3\), (even though it may have an influence), since a high \( T_C \) of about 85 K has been reported for samples without tetragonal distortion, e.g. for nanoparticles\( 11 \) and the LCO/SrLaAlO\(_4\) film discussed in Ref. 12.

Summarizing, the influence of reversible biaxial strain on the magnetization of epitaxially grown LaCoO\(_3\) films has been investigated. The strain-induced increase of \( T_C \) is estimated to be below 4 K/\% of strain in the as-grown state of \( a = 3.88 \text{ Å} \). Our data give evidence for an enhanced magnetic moment of Co ions under tensile strain. Both results confirm that tensile strain strengthens the ferromagnetism in LaCoO\(_3\) films. Dominance of the effect of an enlarged unit cell volume over that of a tetragonal distortion is suggested for inducing ferromagnetism by tensile strain. Soft X-ray absorption experiments, which may clarify the effect of strain on the electronic structure, and particularly on the Co spin state, are in progress.

We thank R. Hühne for stimulating discussions. This work was supported by Deutsche Forschungsgemeinschaft, FOR 520.

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