

## Ferromagnetic order in epitaxially strained LaCoO<sub>3</sub> thin films

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LaCoO<sub>3</sub> films grown epitaxially on (001) oriented (LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr<sub>2</sub>AlTaO<sub>6</sub>)<sub>0.7</sub> substrates by pulsed laser deposition exhibit ferromagnetic ordering below a critical temperature,  $T_c$ , of 85 K. Polycrystalline films of LaCoO<sub>3</sub> prepared in the same way did not show ferromagnetic order down to  $T \approx 5$  K, and their temperature dependent susceptibility was identical to that of bulk LaCoO<sub>3</sub>. The ferromagnetism in epitaxial films is not simply a property of the surface region, rather it extends over the complete film thickness, as shown by the linear increase of the saturated magnetic moment with increasing film thickness. We discuss this surprising result in terms of epitaxial tensile strain via the properly chosen substrate inducing ferromagnetic order.

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### I. INTRODUCTION

Cobaltates have recently received intense interest, both experimentally and theoretically. A large number of interactions in this mixed-valent family of compounds (such as Hund's rule coupling, double exchange, correlation, and crystal field) compete on a similar energy scale and lead to a rich landscape of mutually competing phases, many with unusual macroscopic properties.<sup>1</sup> In this respect, cobaltates are somewhat similar to manganites and also cuprates but do show their own unique flavor—such as the fact that usually two or three spin states are possible. LaCoO<sub>3</sub>, having a Co 3d<sup>6</sup> electron configuration, shows an interesting evolution of its spin state with increasing temperature. Recent experiments<sup>2</sup> have provided strong evidence that the bulk Co<sup>3+</sup> ions are in their nonmagnetic low-spin (LS) ( $t_{2g}^6 e_g^0, S=0$ ) state at lowest temperature, but change to a primarily intermediate-spin (IS) ( $t_{2g}^5 e_g^1, S=1$ ) state in the temperature range 35 K <  $T$  < 100 K (Ref. 3) and further to a mixture of IS and high spin (HS) ( $t_{2g}^4 e_g^2, S=2$ ) states in the interval 300 K <  $T$  < 600 K. On the other hand, the existence of IS has been questioned recently on the basis of x-ray absorption spectroscopy and magnetic circular dichroism.<sup>4</sup> The cross-over between spin states with increasing temperature in undoped LaCoO<sub>3</sub> results from a delicate interplay between the crystal-field splitting  $\Delta_{CF}$ , i.e., the splitting between the  $t_{2g}$  and  $e_g$  energy levels, and the intra-atomic exchange interaction (Hund's rule coupling),  $J_{ex}$ , which leads to a redistribution of electrons between the  $t_{2g}$  and  $e_g$  levels. Since  $\Delta_{CF}$  is found to be very sensitive to the variation of the Co-O bond length,  $r$ , ( $\Delta_{CF} \propto r^{-5}$ ) (Ref. 5), the subtle balance between  $\Delta_{CF}$  and  $J_{ex}$  can easily be influenced by, e.g., hole or electron doping,<sup>6</sup> and chemical or external pressure.<sup>7</sup>

Despite the nonmagnetic LS ground state of LaCoO<sub>3</sub> there are various reports on the existence of either long- or short-range ferromagnetic (FM) order.<sup>8–12</sup> For instance, Menyuk *et al.*<sup>9</sup> have attributed a hysteresis in the magnetization at 1.9 K to the existence of small isolated magnetic regions dispersed in a nonmagnetic matrix. Androulakis *et al.*<sup>11</sup> reported on two FM phases, one with a  $T_c < 10$  K and the

other with 20 K <  $T_c < 100$  K. They suggest that these are caused by the presence of Co<sup>4+</sup> ions associated with La<sup>3+</sup> vacancies. Yan *et al.*<sup>12</sup> have found a FM component with a  $T_c \approx 85$  K whose remanence and coercivity increase with increasing surface/volume ratio of the different samples. They argue that the coordination of surface Co<sup>3+</sup> ions is capable of stabilizing higher spin states, most probably an IS state, and suggest a FM coupling of “surface cobalt atoms.”

In the presence of these conflicting results, the origin of the observed ferromagnetism in LaCoO<sub>3</sub> is a particularly challenging question that motivated the work described in this paper. In order to scrutinize the proposed surface ferromagnetism by Yan *et al.* we have carried out experiments on thin films which inherently show an extremely large surface/volume ratio. In addition, the heteroepitaxial growth of films offers the opportunity to impose a biaxial stress on the film. The lattice mismatch between the film and substrate material which can amount to up to about 2% causes a compressive or tensile strain in the film plane, depending on whether the in-plane lattice parameters of the film are larger or smaller than those of the substrate material. Regarding the elastic properties of oxide materials, a change of the lattice parameters by about 1–2 % usually requires a pressure of several GPa. Since phase transitions in solids, such as structural, magnetic, ferroelectric, or superconducting ones, often depend very sensitively on pressure, physical properties of thin films can thus be changed significantly by epitaxial strain.

Our results to be reported below show that in contrast to polycrystalline LaCoO<sub>3</sub> films which remain paramagnetic down to  $T \approx 5$  K, epitaxial films with the same surface/volume ratio grown on (LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr<sub>2</sub>AlTaO<sub>6</sub>)<sub>0.7</sub> (LSAT) substrates exhibit ferromagnetic order below  $T_c \approx 85$  K. The ferromagnetism extends over the complete film and is not simply restricted to the surface region. We suggest that the ferromagnetic coupling in epitaxial LaCoO<sub>3</sub> films is induced by tensile strain due to the growth on the LSAT substrates.

### II. EXPERIMENTAL

Epitaxial and polycrystalline films of LaCoO<sub>3- $\delta$</sub>  (LCO) were produced by pulsed laser deposition using stoichio-

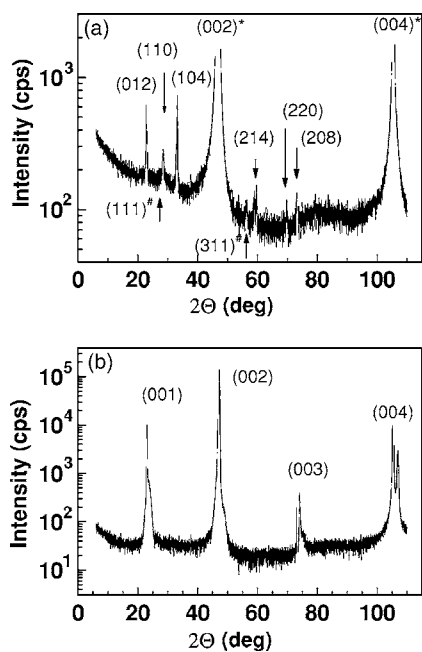


FIG. 1. (a)  $\theta/2\theta$  scan of a polycrystalline LCO film deposited on a (001) oriented LSAT substrate precovered with a 20 nm thick polycrystalline  $\text{CeO}_2$  film. The reflections from LSAT and  $\text{CeO}_2$  are marked by stars and crosses, respectively. The remaining reflections can all be attributed to LCO. (b)  $\theta/2\theta$  scan of an epitaxial LCO film deposited directly on LSAT.

metric sinter targets of LCO. The growth conditions, i.e., substrate temperature,  $T_s$ , oxygen partial pressure,  $p(\text{O}_2)$ , and laser energy,  $E$ , were optimized with respect to crystalline quality and magnetic properties of the resulting films. In order to achieve full oxygenation the samples were annealed after film deposition in a pure oxygen atmosphere of 0.9 bar at 500 °C for about 30 min. The epitaxial films were grown on (001) oriented LSAT substrates. LSAT has a cubic crystal structure with a lattice parameter of  $a \approx 3.87$  Å and therefore allows a cube-on-cube growth of the pseudocubic crystal structure of LCO, with a pseudocubic lattice parameter  $a_c \approx 3.805$  Å. The epitaxial strain due to the lattice mismatch between both materials resulted in a strong formation of cracks in films with a thickness larger than 400 nm. Because of the poor surface quality of such films we only studied films in the thickness range  $25 \text{ nm} < d < 400 \text{ nm}$ . For the growth of the polycrystalline LCO films the LSAT substrates were covered *in situ* with a 20 nm thick polycrystalline  $\text{CeO}_2$  “inhibit” layer prior to the growth of the LCO film.

The films were structurally characterized by x-ray diffraction. For polycrystalline films  $\theta/2\theta$  scans were carried out using a two-circle diffractometer. For the epitaxial films we additionally used a four-circle diffractometer using  $\text{Cu } K\alpha$  radiation to also measure asymmetric Bragg reflections. All films were single phase, showing only LCO-specific  $hkl$  reflections. A typical  $\theta/2\theta$  scan of a polycrystalline LCO film is shown in Fig. 1(a). The polycrystalline films grew with the structure of the bulk material, i.e., a rhombohedral structure ( $R\bar{3}c$ ) with lattice constants of  $a = 5.44$  Å and  $c = 13.10$  Å, corresponding to a pseudocubic lattice parameter of  $a_c \approx 3.805$  Å. For the epitaxial LCO films, see Fig. 1(b), only

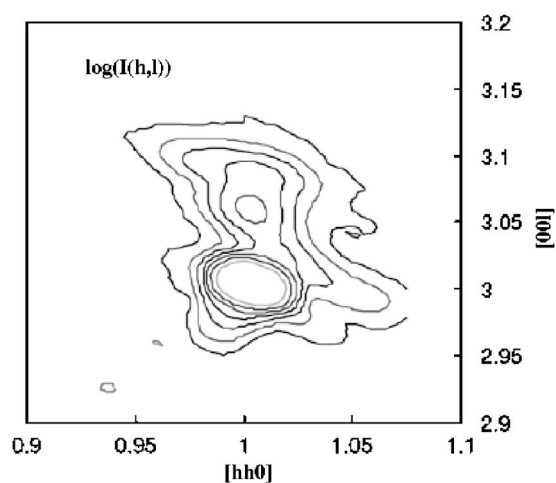


FIG. 2. Reciprocal space map of the 113 LCO film and LSAT substrate reflection. The contour plot is on a logarithmic scale and shows the scattered intensity as a function of the scattering vector  $q$ . Its components are expressed in noninteger Miller indices  $h$  and  $l$  of the LSAT substrate reflection, referring to the azimuth reference [110] and the surface normal [001]. The difference between neighboring contour lines is  $\Delta \log = 0.5$ .

00 $l$  reflections were observed which documents the epitaxial growth of the films. The out-of-plane  $c$ -axis lattice parameter which we extracted from these measurements amounts to  $c \approx 3.81$  Å. The in-plane lattice parameters,  $a$  and  $b$ , were determined from measurements on asymmetric Bragg reflections, i.e.,  $h, k \neq 0$ . Figure 2 displays a reciprocal space map of the 113 LCO film and LSAT substrate reflection. The contour plot on a logarithmic scale shows the scattered intensity as a function of the scattering vector  $q$ . Its components are expressed in noninteger Miller indices  $h$  and  $l$  of the LSAT substrate reflection. The 113 film peak is observed very clearly right above the substrate reflection, i.e., at the same value of  $h = 1$  but, due to the smaller  $c$ -axis lattice parameter, at a larger  $l$  value of about 3.07. From this plot it is quite evident that the in-plane lattice parameters of the film and substrate material are nearly the same. We also carried out further measurements on other reflections from which we could refine  $a \approx b \approx 3.87$  Å and—consistent with our measurements on the two-circle diffractometer— $c \approx 3.81$  Å. So, in contrast to the polycrystalline LCO films the epitaxial films have a pseudotetragonal structure. The tetragonal distortion can be characterized by a parameter defined as  $\Delta_{\text{TG}} = 2(a-c)/(a+c) = 1.5\%$ . The tetragonal lattice parameters and, hence, the tensile strain in the film plane  $\varepsilon_{\text{xx}} = (a - a_c)/a_c \approx +1.7\%$  were almost the same for all the epitaxial films with  $d \leq 400$  nm. Transmission electron microscopy and energy dispersive x-ray (EDX) line-scan analysis with a spatial resolution of about 10 nm on various sample positions confirmed the microstructural and chemical homogeneity of the films. In Fig. 3 we display an EDX line-scan analysis of an epitaxial LCO film. The x-ray fluorescence intensity coming from the  $\text{La}_L$  and  $\text{Co}_K$  shell is plotted as a function of the position within the film plane. The intensity ratio  $I(\text{La}_L)/I(\text{Co}_K)$  is almost constant over the entire distance of about 200 nm, indicating a homogeneous composition. That

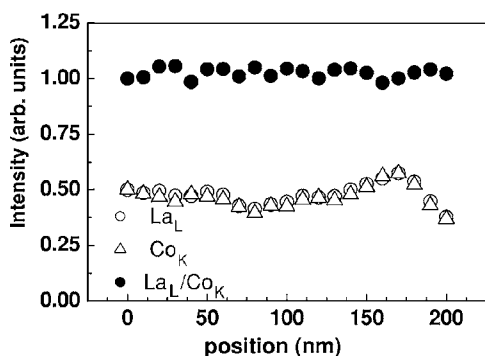


FIG. 3. Energy dispersive x-ray analysis of an epitaxial LCO film. The x-ray fluorescence intensity coming from the  $\text{La}_L$  and  $\text{Co}_K$  shell and the intensity ratio of both is plotted versus the position in the film plane.

the absolute intensity does vary slightly with position is caused by an inhomogeneous sample thickness due to the sample thinning procedure. Rutherford backscattering experiments confirmed the homogeneous and stoichiometric composition of the samples. All this excludes the presence of impurities or the formation of a significant amount of cation vacancies to an extremely high degree.

The magnetic properties of the films were studied using a Quantum Design MPMS SQUID system. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization were measured in the temperature range  $4 \text{ K} \leq T \leq 300 \text{ K}$ . The external field with a strength of  $\mu_0 H = 20 \text{ mT}$  was applied parallel to the film surface. Signals from the substrate materials have been carefully subtracted.

### III. RESULTS AND DISCUSSION

In Fig. 4, we display the FC magnetization,  $M$ , versus temperature,  $T$ , for a polycrystalline and an epitaxial film both with a thickness of about 200 nm. In contrast to the

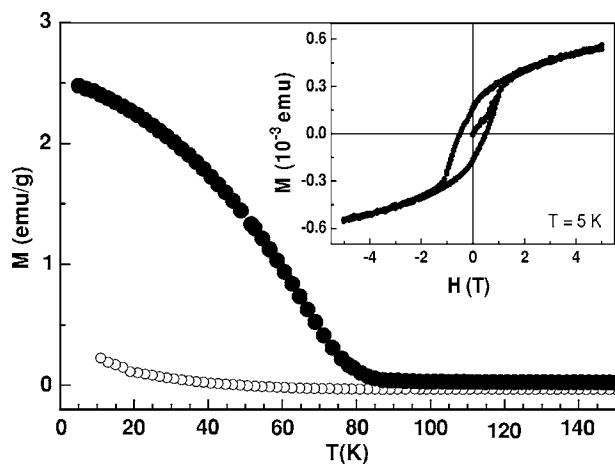


FIG. 4. Field cooled magnetization of polycrystalline ( $\circ$ ) and epitaxial ( $\bullet$ )  $\text{LaCoO}_{3-\delta}$  films ( $d=200 \text{ nm}$ ) measured in an applied field  $\mu_0 H = 20 \text{ mT}$ . The inset shows the magnetic moment of epitaxial  $\text{LaCoO}_{3-\delta}$  at  $T=5 \text{ K}$  as a function of the applied magnetic field.

polycrystalline film which shows a small paramagnetic (PM) contribution to the magnetization only, the epitaxial film clearly exhibits FM order below  $T_c \approx 85 \text{ K}$ . The FM transition appears very broad which is most likely caused by finite size effects due to the small film thickness. The Curie temperature,  $T_c$ , was determined from the onset of the FC magnetization. The effective paramagnetic moment per Co ion,  $\mu_{\text{eff}}$ , was obtained from the susceptibility above  $T=100 \text{ K}$ . For the polycrystalline film  $\mu_{\text{eff}}$  amounted to  $2.0\mu_B$ , where  $\mu_B$  is the Bohr magneton. Assuming a single-electron picture where  $\mu_{\text{eff}} = g_e \times \sqrt{S(S+1)}$ , with the electron  $g$  factor  $g_e = 2$ , this value corresponds to a spin state of  $S=0.65$ . Taking into account a two-level spin system consisting of LS and IS states this corresponds to an occupation of the IS state of 65%, or of 33% of HS assuming occupation of LS and HS states only. Such an occupation of HS states has recently been proposed<sup>4</sup> on the basis of x-ray absorption measurements and seems to be typical for bulk LCO. In contrast, for the epitaxial films we obtained a significantly larger spin value of  $S=1.49$  ( $\mu_{\text{eff}}=3.87\mu_B$ ) independent of the film thickness, which indicates a much stronger occupation of higher spin states. Again, for a two-level spin system this large value for  $S$  can only be achieved with an occupation of 75% HS and 25% LS or a mixing of IS and HS states in a ratio of 1:1, as it is expected for bulk material only well above 300 K. The increased population of higher spin states in the epitaxial films can be well understood from the pressure dependence of the crystal-field splitting,  $\Delta_{\text{CF}}$ , in LCO. As  $\Delta_{\text{CF}}$  rapidly decreases with the increase of the bond lengths ( $\Delta_{\text{CF}} \propto r^{-5}$ ),<sup>5</sup> a larger Co-O bond distance leads to a reduced  $\Delta_{\text{CF}}$  which stabilizes the IS and HS states.<sup>13</sup> Therefore, films under tensile strain should show an increased population of higher spin states. On the other hand, a compression of bond lengths results in a decreased population of higher spin states. In recent experiments, a pressure-induced spin state transition from IS to LS at  $T=300 \text{ K}$  was observed for  $P \geq 4 \text{ GPa}$ .<sup>14,15</sup> Chemical pressure, induced by a partial substitution of  $\text{La}^{3+}$  by the smaller  $\text{Eu}^{3+}$ , leads to a similar stabilization of the LS state.<sup>16</sup> In the inset of Fig. 4 we show the magnetic moment at  $T=5 \text{ K}$  as a function of the magnetic field. The magnetic moment,  $M(H)$ , displays a well-shaped hysteresis loop, corroborating FM order.  $M(H)$  continues to increase above 2 T up to the highest field of 5 T, indicating a PM contribution. A PM contribution has been previously observed in LCO single crystals<sup>12</sup> where it persists to lowest temperatures.<sup>17</sup>

The saturated magnetic moment,  $M_{\text{sat}}$ , corresponds to  $0.4 \mu_B/\text{Co}$  atom after subtracting the unsaturated moment, which has been determined from the linear increase of  $M$  vs  $\mu_0 H$  between 2 T and 5 T. In Fig. 5(a) we plot the magnetic moment of epitaxial LCO films with different film thickness as a function of the magnetic field at  $T=5 \text{ K}$ . Figure 5(b) demonstrates that  $M_{\text{sat}}$  increases with film thickness,  $d$ , and that it does so linearly for  $d > 50 \text{ nm}$ , thus indicating a nearly constant magnetization after the initial stage of film growth. Since for  $d=0$  we expect of course  $M_{\text{sat}}=0$ , the film with  $d \approx 25 \text{ nm}$  exhibits an increased magnetization. The corresponding larger spin state value,  $S$ , might be caused by a higher degree of tensile strain in the film. Even though the

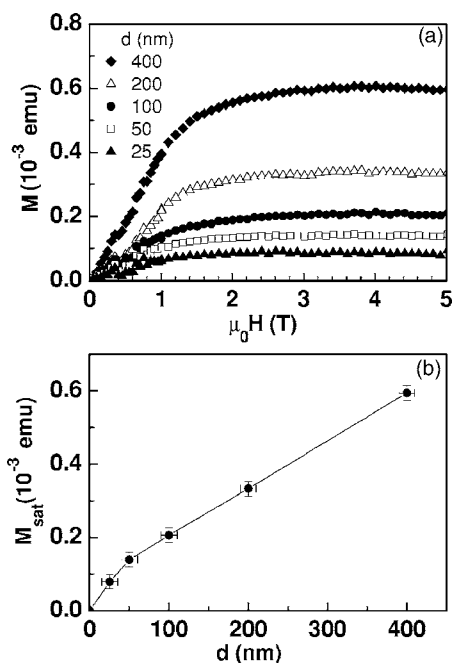


FIG. 5. (a) The magnetic moment at  $T=5$  K as a function of the applied magnetic field (virgin curves) for epitaxial films with different film thickness. The remaining unsaturated moment above 2 T was subtracted from the measurements. (b) The saturated ferromagnetic moment,  $M_{\text{sat}}$ , as a function of the film thickness of epitaxial  $\text{LaCoO}_{3-\delta}$  films.  $M_{\text{sat}}$  was obtained from the measurements in Fig. 3(a) at  $\mu_0 H=5$  T. The line is a guide to the eye.

measured mean lattice parameters of the epitaxial films are nearly the same within the investigated thickness range, the epitaxial strain within the first few monolayers can be expected to be somewhat larger than in the subsequent layers. In addition, the relative contribution of Co surface atoms with possibly larger magnetic moments, which increases with decreasing  $d$ , may play a role. The linear increase of  $M_{\text{sat}}$  vs  $d$  for  $d \geq 50$  nm demonstrates that the FM order in our films is not simply restricted to the surface. It is worth mentioning that the unsaturated magnetic moment unequivocally shows a linear increase with the film thickness as well.

At first sight, a possible explanation of the FM order in LCO might be the presence of  $\text{Co}^{2+}$  or  $\text{Co}^{4+}$  due to unintentional doping which can lead to the well-known ferromagnetic double-exchange interaction with the  $\text{Co}^{3+}$  ions. For instance, a significant oxygen deficiency of  $\text{LaCoO}_{3-\delta}$  with  $\delta \geq 0.05$ , could lead to an electron doping effect as recently observed in  $\text{Ce}^{4+}$  doped  $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$  samples showing a FM exchange interaction with a  $T_c \approx 22$  K.<sup>6</sup> In the case of doping of our epitaxial films, one would expect a variation of  $T_c$  for different oxygen treatments of the films which, however, was not observed in our experiments. We carried out the laser deposition at various oxygen partial pressures,  $1 \text{ mbar} > P(\text{O}_2) > 0.01 \text{ mbar}$ , and at different oxygen annealing times ranging from 0.5 to 2 h, all of them resulting in the same well-defined value of  $T_c \approx 85$  K. This result argues against a doping effect, as does the absence of an oxygen induced effect on the polycrystalline paramagnetic films. Furthermore, an oxygen deficiency should result in the for-

mation of  $\text{Co}^{2+}$  ions. Possible changes in the valence of Co ions can be inferred from the chemical shift in the Co 2p x-ray absorption spectra.<sup>18,19</sup> The preedge region of the multiplet structure around 780 eV is very sensitive to any change in the valence state of the Co ion.<sup>20</sup> We have measured<sup>21</sup> the Co 2p x-ray absorption spectra of non-FM polycrystalline and FM epitaxial LCO films. The spectra did not show significant differences. Therefore, the valence state of Co is similar in both types of samples and thus not responsible for the observed magnetic order in the epitaxial films. The presence of La vacancies which likewise could lead to the formation of  $\text{Co}^{4+}$  as proposed in Ref. 11 can also be ruled out by our Rutherford backscattering experiments, which did not show any significant deviation from stoichiometry. According to the magnetic phase diagram of the hole-doped cobaltates, a doping level as high as 15% of  $\text{Co}^{4+}$  would be needed in order to obtain a  $T_c$  in the range of 85 K. If the formation of  $\text{Co}^{4+}$  is caused by La vacancies, for instance, this would correspond to a nominal composition of  $\text{La}_{0.95}\text{CoO}_3$  which is incompatible with our measurements. In short, we consistently observe in all experiments that the FM order is *not* induced by a doping effect.

As a viable scenario for the observed FM behavior we suggest a strain-induced FM order. Since the tensile strain in the epitaxial LCO films leads to a decrease of  $\Delta_{\text{CF}}$ , the transitions to lower spin states, i.e., HS to IS and IS to LS, are shifted to lower temperatures compared to bulk LCO. This is the reason for the unusually high contribution of IS or HS states observed in the epitaxial LCO films in the temperature range  $100 \text{ K} < T < 200 \text{ K}$  and the significant suppression of transitions from the IS to the LS state below 100 K. IS states are therefore stabilized in the epitaxial films with respect to the polycrystalline films. In bulk LCO the IS state,  $t_{2g}^3 e_g^1$ , is Jahn-Teller (JT) active and a cooperative JT distortion lifts the degeneracy of the  $e_g$  orbitals, triggering long-range antiferrodistortive orbital ordering in the temperature interval 20–300 K.<sup>22–24</sup> This is similar to the situation found in  $\text{LaMnO}_3$  where the JT active  $\text{Mn}^{3+}$  states,  $t_{2g}^3 e_g^1$ , show  $e_g$  orbital polarization into alternating  $(3x^2-r^2)$  and  $(3y^2-r^2)$  orbitals within the  $ab$  plane, which leads to an A-type antiferromagnetic (AFM) ordering.<sup>25</sup> The distortion of the octahedra due to the JT effect can be characterized by the JT parameter,  $D_{\text{JT}}$ , defined as the difference between the long and short Co-O bond lengths normalized to their average. Maris *et al.*<sup>22</sup> have obtained  $D_{\text{JT}} \approx 6\%$  for bulk LCO at room temperature which is similar to, albeit somewhat smaller than, the distortion of  $D_{\text{JT}} \approx 10\%$  found in  $\text{LaMnO}_3$ .<sup>26</sup> We suggest that the JT distortion is strongly suppressed in the epitaxially strained films, where tensile stress exerted by the substrate may lead to a relief of JT strain. Therefore, the splitting of the  $e_g$  orbitals due to the JT effect is also suppressed. This provides a clue to the observation of FM in our epitaxial films: whereas in the case of nondegenerate  $e_g$  orbitals the superexchange gives rise to AFM ordering, in the case of orbital degeneracy magnetic ordering turns out to be FM according to the Goodenough-Kanamori-Anderson rules.<sup>27</sup> FM coupling may also be forced by orbital ordering.<sup>28</sup> Even though the tetragonal distortion of the epitaxial films also leads to a splitting of the  $e_g$  orbitals, the splitting should be much smaller in comparison to the JT

distortion of bulk LCO since  $D_{\text{TG}}$  amounts to 1.5% only. The effect of the remaining tetragonal splitting may be masked by the bandwidth of the  $e_g$  levels due to the strong hybridization between the transition-metal  $3d$  and the oxygen  $2p$  states,<sup>29</sup> resulting in an  $e_g$  orbital that is still effectively non-degenerate. Such a band broadening may, in itself, also facilitate the FM order and is possibly an important ingredient.

#### IV. CONCLUSION

We have shown that FM order can be induced in LCO by strain. The tensile strain in epitaxial LCO films grown on LSAT is instrumental in two ways: (1) It causes a tetragonal distortion of the rhombohedral crystal structure by about

1.5%, probably in conjunction with a decrease of the crystal-field splitting which results in a stabilization of higher spin states. (2) The epitaxial strain strongly suppresses the JT distortion. The near degeneracy of the  $e_g$  orbitals favors FM superexchange and may lead to the FM order observed below  $T_c \approx 85$  K. In contrast to the strain effect, surface induced FM order does not occur, as inferred from a direct comparison with nearly unstrained polycrystalline films that do not exhibit FM order.

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- <sup>17</sup>As a possible reason for the shape of the magnetization curve  $M(H)$  in Fig. 4 one might assume the presence of two magnetic sublattices leading to a ferrimagnetic behavior. In this picture, the kink at about 1 T may be understood as the onset of the magnetic saturation of the first sublattice, and the saturation field of the second sublattice would be above 5 T. Due to the decrease of the slope of  $M$  vs  $\mu_0 H$  above 1 T the coupling of the two magnetic sublattices would be ferromagnetic. Another possibility for the unsaturated magnetization may be the presence of paramagnetic impurities. This appears, however, less likely as the paramagnetic moment is quite large, contributing almost half of the total magnetization at a field  $\mu_0 H = 5$  T.
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