

# Strain-dependent magnetic phase diagram of epitaxial $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin films

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Effects of lattice strain on magnetic behavior of epitaxial  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  thin films grown by  $90^\circ$  off-axis sputtering have been studied. The size of epitaxial strain was varied using four different substrates, i.e., (001)  $\text{LaAlO}_3$ , (001)  $\text{SrTiO}_3$ , (001)  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.65}\text{Ta}_{0.35}\text{O}_9$ , and (110)  $\text{NdGaO}_3$ . The observed magnetism of coherent epitaxial films grown on these substrates, particularly anisotropy and Curie temperature, exhibit strong correlations with lattice strains. Spin reorientation transitions have been observed. The dependence of Curie temperature on the bulk and Jahn–Teller strains has been determined. © 2000 American Institute of Physics. [S0003-6951(00)03217-4]

The doped colossal magnetoresistance (CMR) manganite perovskites exhibit strong coupling between their lattice degrees of freedom and magnetism.<sup>1</sup> Substrate induced strain has been shown to influence the magnetism of epitaxial manganite films strongly,<sup>2–6</sup> specifically magnetic anisotropy, resistivity, and Curie temperature. To date the effects of strain have been studied systematically as a function of film thickness. However, since thin film properties depend on film thickness and growth conditions sensitively and lattice relaxation processes are complex, reproducible correlations between lattice and magnetic order have not been established. An intrinsic study of these effects requires a good control over all key parameters, such that each of them can be varied systematically and its effect is probed, while others kept fixed. In this letter we report a systematic study of the effects of lattice strain on magnetic phase diagram of epitaxial  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  thin films by using four different substrates to vary lattice strains. The experiments were designed to probe the intrinsic effects of both hydrostatic and Jahn–Teller strains, particularly on magnetic phase diagram.

The  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (LSMO) epitaxial films were grown by  $90^\circ$  off-axis sputtering<sup>7</sup> at  $750^\circ\text{C}$  from a stoichiometric target with a 200 mTorr argon–oxygen mixture. Films with thicknesses of 250 and 500 Å were grown epitaxially on four types of substrates, namely (001)  $\text{LaAlO}_3$  (LAO), (001)  $\text{SrTiO}_3$  (STO), (001)  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.35}\text{Ta}_{0.35}\text{O}_9$  (LSAT), and (110)  $\text{NdGaO}_3$  (NGO). The substrates were chosen for their different lattice mismatch with LSMO, ranging from  $-2.0\%$  compressive for LAO, to nearly lattice matched for both LSAT and NGO, and to  $+0.85\%$  tensile for STO, and the thicknesses were selected for obtaining coherent epitaxial interfaces. The three-dimensional (3D) lattice parameters of the films were measured by normal and grazing incidence x-ray diffraction techniques. The bulk-doped manganite LSMO is a distorted perovskite with a pseudocubic lattice parameter ( $a_0^P$ ) of 3.87 Å. In this work Miller indices based on the pseudocubic unit cell are used. Magnetic behavior of

the LSMO films were measured using superconducting quantum interference device (SQUID) magnetometry in the temperature range between 5 and 400 K and field range of  $\pm 5$  T. Magnetic responses along the symmetry directions with respect to the substrate were measured, i.e., for (001) substrates, along the in-plane [100] and [010] directions (parallel to the edges), along one of the in-plane  $\langle 110 \rangle$  directions (the “45°” directions), and along the [001] directions (the “perpendicular” direction).

Our room temperature x-ray diffraction experiments show that the LSMO thin films exhibit a cube-on-cube type of epitaxial arrangement on the substrates. In-plane and out-of-plane lattice parameters of the LSMO epitaxial films and the associated lattice strains, i.e.,  $\epsilon_{100}$  and  $\epsilon_{001}$ , respectively, are shown in Table I. All films are coherent in the growth plane, except the 500 Å one grown on LAO. Films grown on LAO substrates exhibit an out-of-plane tensile strain and a corresponding in-plane compression, and films grown on STO exhibit opposite strain states, i.e., out-of-plane compression and in-plane tension. Owing to their small lattice mismatches, films grown on LSAT and NGO show only a weak out-of-plane tensile strain. The observed behavior is in

TABLE I. In-plane and out-of-plane lattice parameters determined by x-ray diffraction experiments for LSMO films grown on various substrates. The corresponding strain values in percent are shown in the parenthesis. A bulk value of 3.87 Å is used to calculate the strain for the LSMO films. The uncertainties for the lattice parameters are about 0.01 Å in-plane, and 0.002 Å out-of-plane, and the corresponding values for strain are about 0.3% and 0.05%, respectively.

Substrate	Thickness (Å)	Lattice parameter (Å) and strain (%)		
		Out-of-plane	In-plane	Substrate
$\text{LaAlO}_3$	250	3.991(3.1)	3.79(−2.0)	3.793
$\text{LaAlO}_3$	500	3.989(3.1)	3.82(−1.3)	3.793
$\text{SrTiO}_3$	250	3.844(−0.67)	3.90(0.8)	3.905
$\text{SrTiO}_3$	500	3.838(−0.83)	3.90(0.8)	3.905
LSAT	250	3.893(0.59)	3.86(−0.3)	3.868
LSAT	500	3.892(0.57)	3.87(0.0)	3.868
$\text{NdGaO}_3$	250	3.899(0.75)	3.86(−0.3)	3.861
$\text{NdGaO}_3$	500	3.905(0.90)	3.87(0.0)	3.861

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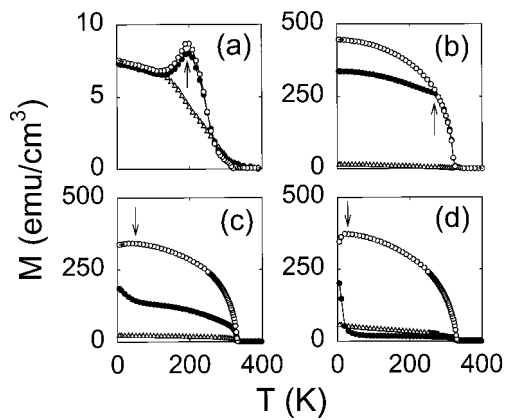


FIG. 1. Field-cooled temperature-dependent magnetization at 5 Oe of 250 Å  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  epitaxial films grown on (a) (001)  $\text{LaAlO}_3$ , (b) (001)  $\text{SrTiO}_3$ , (c) (001) LSAT, and (d) (110)  $\text{NdGaO}_3$  substrates. The responses were measured along three symmetry directions. The directions with respect to the substrate are: for (a) and (b), in-plane [110] (open circles), in-plane [100] (closed circles), and out-of-plane [001] (triangles), and for (c) and (d), in-plane edge directions (circles), and out-of-plane (triangles). Arrows indicate the spin reorientation transitions.

qualitative agreement with results obtained from comparable epitaxial  $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  (LCMO) thin films.<sup>8</sup> Note that the LCMO films with the same thickness as the LSMO samples exhibit lattice relaxation,<sup>8</sup> particularly those grown on LAO substrates, indicating that the LCMO films maybe less able to accommodate strain than their LSMO counterparts. Since the substrate induces an even-parity strain symmetry in the growth plane, the observed 3D strain states by symmetry can be decomposed into a bulk strain  $\epsilon_b = (2\epsilon_{100} + \epsilon_{001})$  and a Jahn–Teller strain  $\epsilon_{JT} = \sqrt{2/3}(\epsilon_{001} - \epsilon_{100})$ .<sup>9</sup> The dependence of magnetic phase diagram on these strain states is the focus of this letter.

The LSMO epitaxial thin films develop spontaneous magnetization at Curie temperatures that are suppressed from the bulk value of  $\sim 370$  K. The field-cooled temperature dependent behaviors along the symmetry directions of 250 Å films grown on four different substrates are illustrated in Fig. 1. As shown in Fig. 1(a), the 250 Å LSMO film grown on LAO substrate develops ferromagnetism below a  $T_C$  of  $\sim 300$  K. The enhanced in-plane magnetization compared to the out-of-plane counterpart indicates the presence of an easy plane anisotropy, which arises evidently from demagnetization effects. As temperature decreases, the in-plane behavior first rises to a peak near 200 K, and then dips down sharply, while the out-of-plane component increases monotonically. The behavior suggests that a spin reorientation transition occurs near 200 K [as indicated by the arrow in Fig. 1(a)], below which perpendicular anisotropy develops. The low temperature perpendicular magnetic anisotropy is confirmed by the field dependent measurements described below. The apparent broad Curie point exhibited by the 250 Å sample is not present in the 500 Å counterpart, and it arises evidently from sample inhomogeneity. As shown in Fig. 1(b), the 250 Å film grown on STO substrate exhibits easy-plane magnetic anisotropy below a  $T_C$  of  $\sim 320$  K. At temperatures below  $\sim 250$  K [indicated by the arrow in Fig. 1(b)], the measured magnetization along the [100] edge direction deviates from the behavior along the [110], indicating that an in-plane biaxial anisotropy develops with in-plane  $\langle 110 \rangle$  axes magneti-

cally easy. The film grown on LSAT substrate also develops easy-plane ferromagnetism in the growth plane below  $\sim 340$  K, as indicated in Fig. 1(c). However, it exhibits a “distorted” biaxial anisotropy with the easy axes in the growth plane between the [100] and  $\langle 110 \rangle$  directions. The observed easy-axes remain relatively constant below  $T_C$  at about  $20^\circ$  from [100], and rotate towards the  $\langle 110 \rangle$  directions below  $\sim 50$  K to about  $30^\circ$  from [100] at 5 K. The observed anisotropy can be described as a superposition of a uniaxial anisotropy along [100] and a biaxial anisotropy along the two  $\langle 110 \rangle$  directions. In this context, the spin reorientation can be understood as a change of relative strength of the uniaxial and biaxial anisotropies. Finally, the film grown on NGO substrate develops ferromagnetism below  $\sim 340$  K with an in-plane uniaxial anisotropy along one of the edges of the substrate, as indicated in Fig. 1(d). Below  $\sim 30$  K, a weak biaxial anisotropy similar to that observed in the LSAT sample develops. In other words, samples grown on LSAT and NGO substrates exhibit both uniaxial and biaxial anisotropies in the growth plane with their relative strengths that are temperature dependent, e.g., enhanced strength of biaxial anisotropy at low temperatures. The observed in-plane uniaxial anisotropy has not been seen previously in manganite thin films. While the origin of this behavior is not clear at the moment, it may arise from substrate miscut or the (110) symmetry of the substrate in the case of NGO. The corresponding 500 Å films show the same qualitative behaviors. The observed low temperature magnetic anisotropies, particularly for samples grown on LAO and STO, are similar to those observed in comparable LCMO thin films.<sup>4,5</sup> However, the observed spin reorientation transitions appear to be a general feature of LSMO epitaxial thin films, which is not present in the LCMO thin films<sup>4,5</sup> and has not been reported in LSMO films either.<sup>2,3</sup>

Field dependent magnetic measurements of LSMO films grown on LAO substrates confirm the presence of perpendicular magnetic anisotropy at low temperature. Figure 2(a) illustrates the behavior at 5 K for a 250 Å film. At low temperatures, the perpendicular hysteresis loops after demagnetization corrections are nearly square, and the in-plane components exhibit low remanence and high saturation field (about 1 T at 5 K). The out-of-plane coercive field is about 2 kOe at 5 K, and its in-plane counterpart is about 500 Oe, and they decrease with increasing temperature. The saturation magnetization  $M_{\text{sat}}$  is about 200  $\text{emu}/\text{cm}^3$  for the 250 Å sample, and it is about 260  $\text{emu}/\text{cm}^3$  for the 500 Å sample, both of which are substantially suppressed from the bulk value. In contrast the films grown on STO exhibit easy-plane magnetic anisotropy at low temperatures, as illustrated in Fig. 2(b). The nearly square in-plane loops, and the low remanence and high saturation field ( $\sim 1.5$  T at 5 K) of the out-of-plane component confirm this observation. The presence of a weak biaxial anisotropy along the in-plane  $\langle 110 \rangle$  axes ( $45^\circ$  directions) is indicated by the low field in-plane behavior, as illustrated in Fig. 2(b) inset. The observed  $M_{\text{sat}}$  is about 500  $\text{emu}/\text{cm}^3$ , and the coercive field is about 20 Oe. The observed field dependencies, including the values for  $M_{\text{sat}}$ , are similar to those of the LCMO,<sup>5</sup> particularly for those with comparable strain values rather than the film thickness. The behavior of the LSAT sample, as shown in

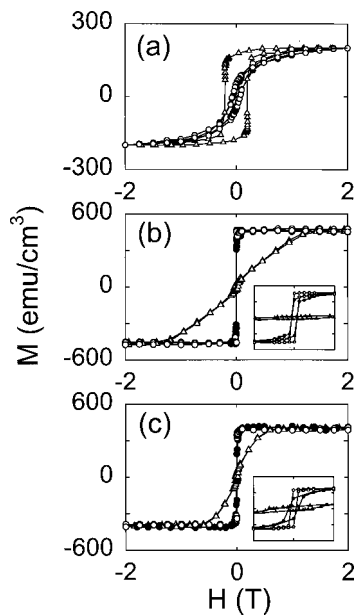


FIG. 2. Hysteresis loops at 5 K of 250 Å  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  epitaxial films grown on (a)  $\text{LaAlO}_3$ , (b)  $\text{SrTiO}_3$ , and (c) LSAT (001) substrates. For (a) and (b) the responses were measured along the in-plane [110] (open circles), in-plane [100] (closed circles), and [001] (triangles) of the substrate, and for (c) the measurements were along the in-plane [100] (open circles) and [010] (closed circles), and the out-of-plane [001] (triangles) of the substrate. Insets are the corresponding low field responses with a field range of  $\pm 400$  Oe.

Fig. 2(c), confirms the presence of a distorted easy-plane anisotropy. The in-plane biaxial easy axes are about  $30^\circ$  with respect to the [100] direction, as indicated by the low field behavior shown in Fig. 2(c) inset, particularly the remanent magnetization for the responses along [100] and [010] orientations. Its out-of-plane saturation field is less than that of the STO sample, about 5 kOe, indicating a weaker easy-plane anisotropy compared to the STO sample. The samples grown on NGO exhibit the same qualitative field dependent features as those of the LSAT samples, but the strong magnetism of the NGO substrate precludes any quantitative analysis.

The observed magnetic behavior as shown in Figs. 1 and 2 when compared to the measured lattice strains as shown in Table I exhibit strong correlations. First we look at magnetic anisotropy. The LSMO samples grown on LSAT and NGO are nearly strain free, and they exhibit distorted biaxial anisotropy in the grown plane. The samples grown on LAO experience a uniaxial tensile strain, which produces a perpendicular easy axis, and the samples grown on STO are under a biaxial tensile strain in the growth plane, which leads to a biaxial easy plane anisotropy. These findings reveal that the magnetic anisotropy of the LSMO thin films is very sensitive to the symmetry and morphology of the substrate, and that lattice strains can induce an additional anisotropy along the direction of tensile strain.

For weak strains,  $T_C(\epsilon_b, \epsilon_{JT})$  can be expanded in powers of the strains. Cubic symmetry of LSMO requires that the leading terms in  $\epsilon_b$  and  $\epsilon_{JT}$  be linear and quadratic, respectively.<sup>6,9</sup> This gives

$$T_C(\epsilon_b, \epsilon_{JT}) = T_C(0,0)(1 - a\epsilon_b - b\epsilon_{JT}^2). \quad (1)$$

In this expansion the respective coefficients for the strains are  $a = 1/T_C(0,0)dT_C/d\epsilon_b$  and  $b = 1/[2T_C(0,0)]dT_C/d\epsilon_{JT}$ .<sup>9</sup>

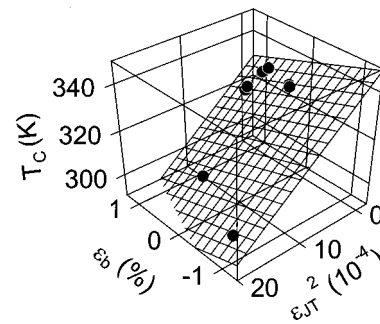


FIG. 3. Curie temperatures of 250 and 500 Å  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  epitaxial films as a function of bulk strain,  $\epsilon_b$ , and square of Jahn–Teller strain,  $\epsilon_{JT}^2$ . The plane corresponds to a fit of the data given by Eq. (1).

The observed  $T_C$  values have been plotted with respect to  $\epsilon_b$  and  $\epsilon_{JT}^2$  in Fig. 3 and fitted using Eq. (1). The parameters obtained from the fit are  $T_C(0,0) = 334 \pm 2$  K,  $a = 2.2 \pm 0.6$ , and  $b = 70 \pm 6$ . The  $T_C(0,0)$  corresponds to the value for a strain free epitaxial thin film, and the value from the fit is suppressed from that of the bulk, indicating that the intrinsic thin film behavior may be different from that of the bulk. However, the suppression may also be due to a change in the composition at these coverages, e.g., oxygen deficiency. The hydrostatic effects that give rise to the linear  $\epsilon_b$  dependence have been studied extensively.<sup>6,9,10</sup> The value of 2.2 agrees with those obtained from optimally doped samples.<sup>10</sup> In contrast the value for  $b$  obtained from the fit corresponds to a first systematic observation, using coherent films based on measured lattice parameters, but it is about ten times smaller than those estimated from other manganite epitaxial films.<sup>6,9</sup> Further studies with fixed film thickness and continuously “tunable” lattice strains are necessary to elucidate this.

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