Magnetoelastic coupling in $La_{2/3}Sr_{1/3}MnO_3$ thin films on $SrTiO_3$

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Clamping of epitaxial $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) magnetic thin films on $SrTiO_3$ (STO) substrates is shown to promote a clear modification of their magnetic properties at the STO cubic-tetragonal transition. Two distinct mechanisms triggered by the STO transition, namely magnetic domain pattern reconstruction and creation of regions within the magnetically soft LSMO with enhanced magnetic anisotropy, are proposed to be behind the observed anomalous magnetic responses at low ac-magnetic field and at high dc-field, respectively. The persistence of these anomalies in LSMO films as thick as 220 nm shines new light into the magnetoelastic coupling mechanisms across interfaces.

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I. INTRODUCTION

Epitaxial thin films can be subjected to strong elastic strain due to structural mismatch with respect to substrates that may radically modify their intrinsic properties. In particular, cubic substrates, such as $SrTiO_3$ (STO), may induce a biaxial strain, either compressive or tensile, on the growing film that most commonly results on a tetragonal distortion of its structure. In addition to bond-length shortening or expansion, the extreme flexibility of the oxygen coordination polyhedra in the perovskite ABO_3 structure allows complex patterns associated with rotations of the BO_6 building units. Whereas exploitation of substrate-induced strain engineering to tailor properties of films is very mature, manipulating the relative orientation of the coordination polyhedron to modify the properties of thin films, in spite of promising predictions,[1–4] has remained quite unexplored.[5]

STO, the most common substrate for epitaxial growth of oxides, offers a unique opportunity to study such an effect. Indeed, STO is a cubic perovskite at room temperature, but it has a structural transition to a tetragonal phase at $T_{STO} \approx 105$ K. This phase transition is directly connected to a phonon softening starting at temperatures well away from T_{STO}.[6] Of relevance here is that the TiO_6 octahedra rotate around a former cubic axis and, as the oxygen ions remain in the faces of the unit cell, an expansion is produced in the direction of the rotation axis (c), and a shortening takes place in the perpendicular direction (a), thus producing a tetragonal unit cell. Domains with three different orientations of the tetragonal c axis are formed, leading to a complex pattern of twins (changes of orientation of a and c axes) and antiphase (adjacent regions of opposite rotation patterns) structural domains. This transition involves small changes of lattice parameters, as oxygen displacements are less than 0.03 Å.

Because of the delicate balance between spin, charge, and lattice couplings, colossal magnetoresistance manganite thin films are optimal candidates to prove the small effects associated with the cubic-to-tetragonal transition of STO on their magnetotransport properties. Indeed, recent investigations on $La_{1-x}A_xMnO_3$ (A = Sr, Ca) thin films grown on STO have reported subtle changes on their magnetic and electric properties, and two limiting different scenarios have been proposed: a dynamic one, in which the softening of the STO lattice couples to spin excitations of the $La_{1-x}Sr_xMnO_3$ film,[7] and a static response linked either to polyhedra deformation or rotation and twining.[8–11] Whereas the former points to a phenomenon limited to the immediate vicinity of the manganite-STO interface, the latter may in principle propagate much deeper in the films. Thus, a general accepted picture of this magnetoelastic coupling across the manganite-STO interface is still lacking.

Here, we report on two anomalous magnetic responses of $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) thin films observed close to the phase transition of STO. Two distinct mechanisms, namely the creation of regions with enhanced magnetic anisotropy and a magnetic domain pattern reconstruction, are proposed to be responsible for the anomalous magnetic responses at high dc-field and low ac-magnetic field, respectively. From the experiments, we infer a dominant role of STO-triggered static modification of the LSMO microstructure that extends deep into the films, rather than an interface dynamic coupling of the soft modes of STO to the LSMO lattice or a coherent static coupling of deformed TiO_6/MnO_6 octahedra confined to the STO-LSMO interface.

II. EXPERIMENTAL

Epitaxial LSMO thin films of thickness (t = 17, 26, and 220 nm) were grown on STO(001) single crystalline substrates by pulsed laser deposition.[12] X-ray diffraction indicates that films are fully epitaxial, with c axis perpendicular to substrate surface and the in-plane [100]LSMO//[100]STO epitaxial relationship (pseudocubic notation is used). Reciprocal-space maps collected with a Bruker-AXS D8 diffractometer show that films are fully strained (tensile) on the STO substrate. Within the experimental resolution, maps collected around the (204) and (024) reflections indicated a tetragonal structure with no evidence of the rhombohedral bulk structure. Both dc and ac (amplitude h_{ac} = 1–15 Oe, frequency range 33–3,333 Hz) magnetic measurements were performed using a Superconducting Quantum Interference Device (SQUID) magnetometer and a Physical Properties Measurement System (PPMS) susceptometer from Quantum Design, respectively. Special care was taken to account for the remnant field

of the superconducting magnet since it has been realized to be crucial for the ac-susceptibility response. In what follows, we will focus mainly on the data of the thinnest LSMO films. Data for the thickest film (220 nm) will provide additional support for some conclusions.

III. RESULTS AND DISCUSSION

A. Low field ac-susceptibility response

The temperature dependence of the in-phase (χ') and out-of-phase (χ'') components of the low-field ac-susceptibility for the 26-nm film is shown in Figs. 1(a) and 1(b) (insets) for h_{ac}//[100] and h_{ac}//[110]. The film orders magnetically below 320 K (a value typical of high-quality films), as evidenced by appearance of nonzero χ'' below this temperature and a rapid increase of χ', which forms a peak just below the transition—see the insets of Fig. 1. At lower temperatures, another peak develops in both components, reflecting the evolution of spontaneous magnetization and anisotropy; the enhanced susceptibility (χ') and losses (χ'') indicate the formation and freezing of the magnetic domain structure at a temperature slightly below the Curie temperature, as also suggested by the strong frequency dependence (not shown) of susceptibility between the two peaks. It can be noticed that the susceptibility measured along [110] is substantially smaller than along [100], in agreement with the biaxial anisotropy of the LSMO film with ⟨100⟩ easy axes, as we have confirmed by angular-dependent magneto-optic measurements. We recall that, in general, there are two distinct contributions to the low field ac susceptibility,[13] namely originating from domain magnetization rotation or from domain wall displacement—while for ac field parallel to the domain magnetization, the latter is zero; the former contribution is maximum. Furthermore, one notices that both components of the susceptibility become small and featureless in a broad temperature region extending from ∼200 K to ∼110 K. This gradual reduction of susceptibility with decreasing temperature reflects the increase of magnetic anisotropy and progressive decrease of magnetic domain walls mobility when lowering temperature.

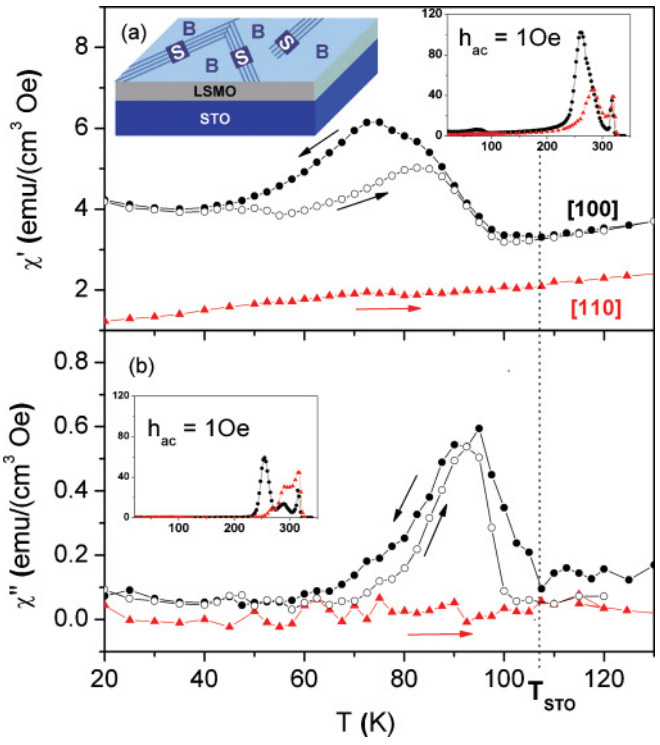

FIG. 1. (Color online) Temperature dependence of (a) the real and (b) imaginary components of ac susceptibility, measured at 1111 Hz, for the 26-nm LSMO film. Black circles correspond to ac field (h_{ac} = 3 Oe) applied along [100] crystallographic direction, red triangles correspond to ac field (h_{ac} = 1 Oe) along [110] direction. Dotted line marks the STO structural transition temperature. Arrows indicate the way of changing temperature. In the insets, full temperature range for the measurements is shown. Sketch in (a) illustrates the *S* and *B* magnetic domain patterns as described in text.

In what follows, we will limit our discussion mostly to the ac-magnetic response in the vicinity of the STO structural transition. We observe that, while for h_{ac}//[110], the susceptibility changes smoothly on crossing the STO structural transition, there is a clear rise of both components on decreasing the temperature just below about 105 K when h_{ac}//[100], and they go through a maximum at lower temperatures [Figs. 1(a) and 1(b)]. Remarkably, this ac response is hysteretic below T_{STO}, depending on whether the data are recorded on cooling or on warming the sample.[14] We note that aging effects, revealed by a suppression of the anomalous ac-magnetic response after many thermal cycles, are observed.

The observation of $\chi'(T)$ and $\chi''(T)$ susceptibility peaks developing close to T_{STO} strongly suggests that they are signatures of changes in the magnetic structure related to the substrate structural changes. The onset of these peaks occurring at temperatures slightly lower than bulk STO transition (105 K) may be related to the modification of the structural transition in a region close to the interface, as shown in Ref. 15. In principle, three different mechanisms can be considered to account for the observed response: (i) twins and antiphase boundaries created in the STO substrate at T_{STO} may promote the occurrence of stripe regions (*S*) in the film, displaying a stripe pattern of magnetic domains with a small out-of-plane component of the magnetization alternatively pointing up or down, which in turn form new magnetic domain boundaries.[8] These *S* regions are formed within the preexisting large regions (*B*) with in-plane magnetization; (ii) below T_{STO}, *B* regions coexist and are bounded by magnetic stripes of *S* regions [see sketch in Fig. 1(a) (inset)], discussed in (i), as observed by magneto-optical microscopy.[8] The particular magnetic domain pattern in these regions should not be identical to that existing above T_{STO}, since domain reconstruction must occur after changes in the domain boundary conditions and the magnetostatic energy triggered by *S* regions. (iii) The structural changes of the substrate may propagate into the clamped film, thus producing concomitant changes in the Mn-O-Mn magnetic interactions and consequently its magnetic anisotropy.

According to Ref. 8, the stripe pattern of scenario (i) could form along the ⟨100⟩ directions with a small out-of-plane magnetization component, resulting from the substrate-induced strain. Data reported for $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) show that the stripe pattern remains stable at least up to 250 Oe, indicating a relatively robust out-of-plane anisotropy. Thus, at odds with data of Fig. 1, at small fields (∼1 Oe),

the ac susceptibility should not be enhanced, regardless of the number of magnetic stripes. Note, however, that the presence of a sizable out-of-plane anisotropy (the anisotropy field of the stripes should be larger than the demagnetizing field, which is of the order of 4 kOe, to induce an out-of-plane component of magnetization) is coherent with a reduction of the in-plane magnetization, even at rather high applied fields, in agreement with our experimental data at dc fields, which will be discussed later.

In scenario (ii), the in-plane magnetic reconstruction in B regions should produce a new pattern of magnetic domains and domain walls. Concomitant with domain reconstruction, a large susceptibility should be expected. This is in agreement with the experimental data (Fig. 1). Moreover, as structural changes in STO at T_{STO} are minute ($\Delta a/a \approx 10^{-2}\%$),[15,16] the in-plane magnetic anisotropy of LSMO is not expected to vary significantly, and consequently, the in-plane magnetic axes and the overall domain orientation should remain in-plane, as they were above T_{STO}. Therefore the ac-susceptibility anisotropy at $T < T_{STO}$ should mimic that observed at $T > T_{STO}$. This is in agreement with experimental data (Fig. 1) showing that in both temperature ranges χ' remains larger for h_{ac}//[100] than for h_{ac}//[110].

Finally, although from the available experimental data it is not possible to elucidate if mechanism (iii) is relevant, some hints can be obtained from the consideration that unit cell variations in STO are of only about $10^{-2}\%$. If the changes in LSMO are of about this value, the (Mn-O-Mn) superexchange/double exchange interactions should be modified by a negligible amount, thus with minor impact on the magnetic anisotropy of LSMO, as argued above. In other words, the rather small changes in the cell parameters in STO at the structural transition do not significantly modify the superexchange interactions or the magnetoelastic energy of the B regions. Instead, we claim that, as a result of substrate-induced twining, the domain pattern in LSMO changes. Strain effects at twins create an out-of-phase component of magnetization in the S regions (identified in Ref. 8), and subsequently, at T_{STO}, the change in the boundary conditions changes the domain pattern within the B regions.

Attributing the low-field ac-susceptibility response to domain reconstruction at B regions is further supported by the effect of superimposing a dc-magnetic field. As seen in Fig. 2 for the 17-nm-thick film, the ac-susceptibility $\chi'(T)$ anomaly below T_{STO} is greatly suppressed upon superimposing a rather small dc field (≈20 Oe) parallel to h_{ac}//[100]. It is worth noting that the dc-bias field similarly suppresses the high-temperature $\chi'(T)$ peak attributed to formation of domain structure just below the Curie temperature. We thus conclude that the enhanced ac susceptibility close to T_{STO} is mainly dictated by domain reconstruction of scenario (ii), rather than by the magnetic stripes at the twins [scenario (i)] or by changes in magnetic interactions within the LSMO layer [scenario (iii)].

B. Response at dc fields

We turn now to the dc magnetization. The field and temperature dependencies of the magnetization of the 26-nm LSMO film are shown in Figs. 3(a) and 3(b), respectively. Data in Fig. 3(a) indicates that the film has a saturation

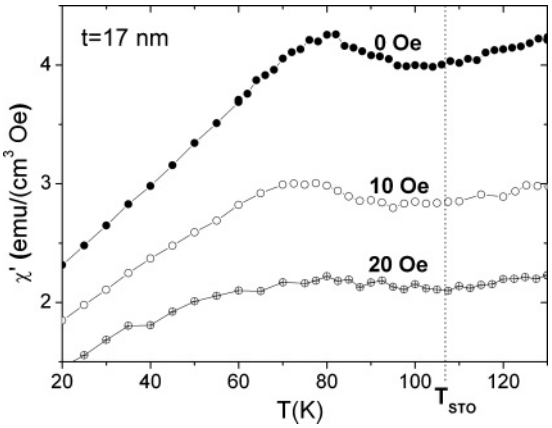

FIG. 2. The real component of ac susceptibility, χ', along [100] direction for the 17-nm-thick LSMO film under superimposed dc field in the same direction as the ac field. Dotted line marks the STO structural transition temperature.

magnetization of 450 emu/cm^3 at 5 K, very close to that expected for bulk $La_{2/3}Sr_{1/3}MnO_3$. Although the temperature dependence of the magnetization $M(T)$ appears to be smooth and featureless at all temperatures, a close inspection reveals a dip at $T \approx T_{STO}$, definitively more apparent when a smaller field is used in the measurements [Fig. 3(c)]. This feature in the magnetization is visible for different magnetic fields and for different orientations ([100], [110], and [001]) and is better appreciated in the derivatives dM/dT vs T, shown in Fig. 3(d). It is important to notice that the magnetization dip (∼100 K) is still well visible even at $H = 1$ kOe, while at low temperature (5 K), the technical saturation field is about 300 Oe, and the coercivity field is only about 15 Oe [see the hysteresis loop in Fig. 3(a)]. This observation indicates that the magnetization dip is not triggered by the overall magnetic response of the film. Interestingly enough, the dip in $M(T)$ is still observed for the thickest film [220 nm, Fig. 3(e)], signaling that the effect of strain propagates deep in the film.

Comparison of the ac-susceptibility data (Figs. 1 and 2) and dc magnetization (Fig. 3) is intriguing. Their very different responses to the driving fields (small h_{ac} and large H) suggests that, although the $\chi'(T)$ and $\chi''(T)$ peaks and the dc-magnetization dip both appear at $\sim T_{STO}$, their origins should be different. Furthermore, whereas the peculiarity in the ac-magnetic response appears only along the [100] crystallographic orientation, the dc-magnetization dip was observed for fields applied along the in-plane [100], [110], and out-of-plane [001] directions. The magnetic domain reconstruction within B regions, which we proposed to be behind the ac-magnetic response at $\sim T_{STO}$, cannot be the primary reason causing the dc-magnetization dip, since the latter effect persists to fields at which, in principle, no domain structure should survive.

However, the presence of stripe domains with out-of-plane strain-induced magnetization, as that observed in S regions of LCMO,[8] provides a natural explanation for the reduction of magnetization at T_{STO}. Our out-of-plane dc-field measurements (not shown) confirmed the existence of hard magnetic regions (coercive field of about 500 Oe) with a noticeable out-of-plane component of the magnetization (remnant

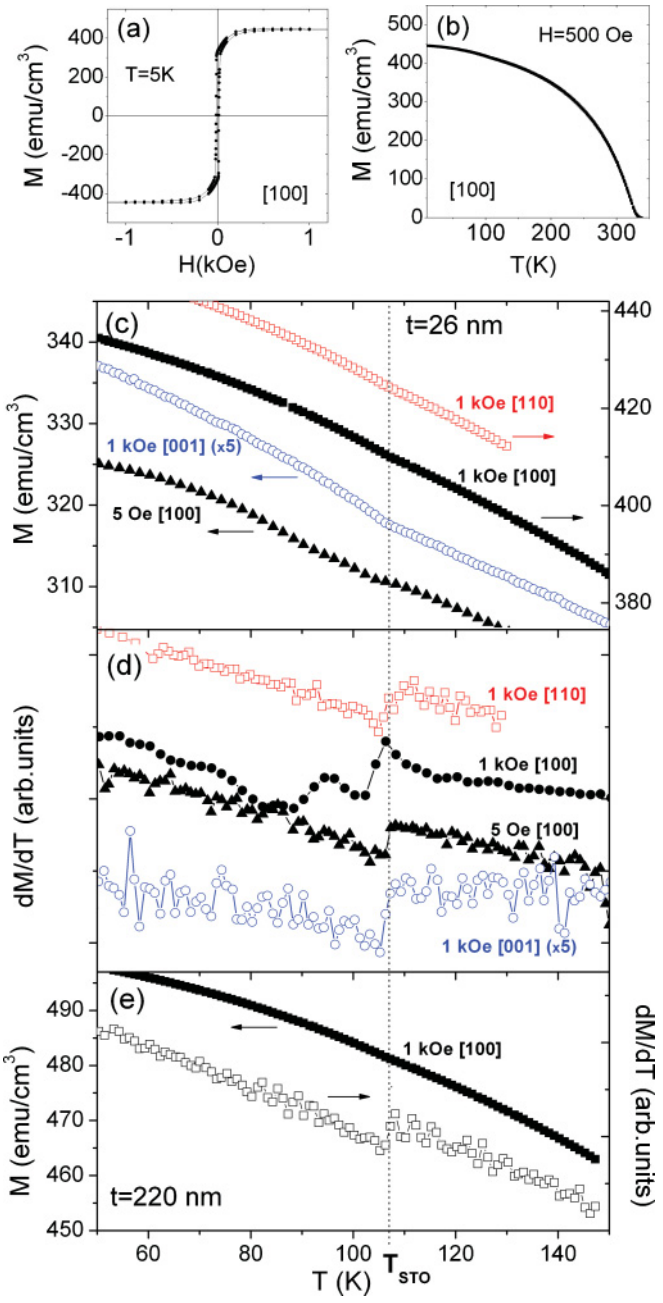

FIG. 3. (Color online) (a) Field and (b) temperature dependence of magnetization measured at $T = 5$ K and $H = 500$ Oe, respectively, along the [100] in-plane direction for the 26-nm LSMO film. (c) Temperature dependence of magnetization for 26-nm LSMO film. Black triangles and squares correspond to 5 and 1,000 Oe field, respectively, applied along [100] direction. Red empty squares correspond to 1,000 Oe field applied along [110] direction. Blue empty circles correspond to 1,000 Oe applied along out-of-plane [001] direction (data multiplied by a factor of five). (d) Derivatives of the curves from panel (c). (e) Temperature dependence of magnetization for the 220-nm film (left axis) and corresponding derivative dM/dT (right axis) under an applied field of 1,000 Oe along [100] direction. Dotted line marks the STO structural transition temperature.

magnetization of about 50 emu/cc). The stripe domain pattern could result from a substrate-driven strain release mechanism within the LSMO film, rather than from the twinning resulting from a tetragonal-to-orthorhombic structural transition, as proposed in LCMO.[8] In this picture, across the closure domains formed at the new domain boundaries, strongly antiferromagnetically coupled regions of antiparallel domains could appear. Such rigid noncollinear magnetic moment alignment would cause the reduction in magnetization at fields even higher than the technical saturation field, as found at antiphase boundaries in magnetite or other insulating oxides.[17–19]

IV. CONCLUSIONS

The identification of two distinct mechanisms contributing to the magnetic response of LSMO films epitaxially clamped on STO substrates is based on the remarkable differences we observe in low-field ac- and high-field dc-magnetic measurements. Ziese *et al.*[9] recently reported on high harmonics ac-susceptibility data of LSMO//STO films and concluded that the observed response at temperatures below T_{STO} was related to the formation of domains in LSMO resulting from the domain formation in the STO substrate at T_{STO}.[20] Segal *et al.*[7] have recently reported a detailed analysis of the magnetic response of $La_{1-x}Sr_xMnO_3$ ($x = 0.47$) thin films (~11 unit cells; ~4.4 nm). They detected significant changes of magnetization and resistivity at $T \approx T_{STO}$. It was claimed that, when approaching T_{STO}, the magnetization is reduced below the expected monotonic $M(T)$ dependence, and it was argued this reduction was caused by the softening of phonons of STO that couple (and soften) magnons in the LSMO film. Density functional theory combined with Monte Carlo calculations were used to estimate the depth of the correlated motion of oxygen ions in the LSMO film as a result of the softening of the STO lattice. It was shown that it decays exponentially into the LSMO layer with a decay length of about 2–3 u.c. Our results, showing that the effects produced by the STO substrate on the magnetic response of the LSMO films—and particularly the magnetization changes at T_{STO} are well visible in a 26-nm-thick film [Figs. 3(c) and 3(d)] and even in an LSMO film as thick as 220 nm [see Fig. 3(e)]—indicate that the proposed dynamic coupling of rotating octahedra across the STO//LSMO interface does not appear to describe the data here reported, as the magnetic depression caused in the LSMO film by the STO structural changes, accordingly to the reported decay length, would affect an interfacial layer which corresponds to less than 0.5 % of the film volume in the case of the 220-nm sample, thus being undetectable for our SQUID equipment.

In summary, our data show that the structural transition in the STO and the concomitant twinning affect the magnetic properties of manganite thin films. Two distinct mechanisms triggered by the STO transition, namely the creation of regions of enhanced magnetic anisotropy within the magnetically soft LSMO matrix and the accompanying magnetic domain reconstruction of the latter, are proposed to be behind the observed anomalous magnetic responses at high dc field and low ac-magnetic field, respectively. The observed effects result from static deformations of the microstructure rather than from dynamic coupling of the soft modes of STO to the magnetic LSMO lattice. Anyhow, these effects indicate a remarkable magnetoelastic coupling dramatically enhanced by the extreme sensitivity of manganites to bond and magnetostatic modifications. The observation that LSMO films as thick as

220 nm are sensitive to the tiny modifications of the STO substrate should help to understand the microscopic origins of interface-mediated coupling in oxide heterostructures. Direct studies of the evolution of the magnetic domain structure at low temperatures are needed to validate the scenario proposed in this paper.

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