Magnetic and electronic structure of ultrathin $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films at half doping

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The magnetic, transport, and electronic properties of ultrathin epitaxial $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) films at near half doping ($x = 0.47, 0.50$, and 0.55), grown under different misfit strains on $\text{SrTiO}_3(001)$ and $\text{La}_{0.18}\text{Sr}_{0.82}\text{Al}_{0.59}\text{Ta}_{0.41}\text{O}_3(001)$ (LSAT) substrates, are investigated. We find that all films exhibit metallic behavior below the magnetic critical temperature, while the magnetic properties change markedly with both doping and strain. However, while increased doping favors antiferromagnetic ordering, strain is the driving mechanism for the change in the magnetic properties, where with increasing tensile strain the magnetic ground state changes from ferromagnetic to antiferromagnetic at a critical lattice misfit threshold of about -1% . The bulk magnetometry data are confirmed by x-ray magnetic circular dichroism spectroscopy, while x-ray magnetic linear dichroism measured at room temperature demonstrates a progressive change in the orbital occupancy with increasing misfit strain from out of plane to in-plane, leading to a preferred antiferromagnetic metallic state at larger tensile strains.

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I. INTRODUCTION

The properties of the doped manganites have been the subject of intensive investigation since their discovery in the early 1950s [1], due in large measure to the rich and complex behavior typical of these systems. Renewed interest has arisen with the development of techniques for the growth of high-quality epitaxial thin films [2–4] and following the discovery of the so-called “colossal” magnetoresistance (CMR) effect [5–9], which has since become a moniker for the doped manganites. The rich electronic, magnetic, and electric properties of this class of compounds, and their sensitivity to external control parameters, are features that are particularly interesting from an applied physics perspective, while their intricate physical behavior makes them a model system for studying the role of strong electron correlations. There is therefore a large interest in understanding the properties of this class of materials from both applied and basic science perspectives.

Despite the sizable body of work already carried out on the doped manganites, the large phase space associated with these systems makes a full characterization and understanding of these systems challenging. In addition to chemical doping, film growth by epitaxy allows a fine control over thickness and strain [10], parameters which have a strong effect on the electronic properties of the manganites. Strain induces changes in the O-Mn bond angles and lengths, leading to modifications in the electron hopping rates and in the electronic structure. Reduction in thickness is expected to lead to the emergence of low dimensionality effects due to the reduction in coordination number of the atoms at the interface; in addition, extrinsic factors, such as interdiffusion at interfaces, modified cation and oxygen stoichiometry, and other defects can lead to strong deviations to the bulk magnetic and electric properties [11–15]. Further complexity arises with the emergence of intrinsic interfacial

effects [16,17]; strain and couplings between phonon, magnetic, and charge degrees of freedom have been found to modify the behavior of doped manganite films quite markedly. Examples include the observation of a charge-mediated magnetoelectric coupling in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) and $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$ -ferroelectric heterostructures [18–23], the presence of a spin exchange-mediated magnetoelectric coupling in $\text{BiFeO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ heterostructures [24], and the observation of a strong phonon-mediated modulation of the magnetic and transport properties at $\text{La}_{0.53}\text{Sr}_{0.47}\text{MnO}_3/\text{SrTiO}_3$ interfaces [25]. In the latter case, the soft phonon mode of the SrTiO_3 substrate at the cubic to tetragonal phase transition couples resonantly to the phonon modes in LSMO to induce modulations in the resistivity due to enhanced electron-phonon scattering at the interface, an effect that, while present at lower Sr dopings, is very strong at $x = 0.47$. This phenomenon also showcases the sensitivity of the doped manganites at half doping, where the phase diagrams tend to be particularly complex [26–30]. In this context, we investigate here the transport, magnetic, and electronic structure of epitaxial ultrathin LSMO films at near half doping grown on SrTiO_3 and $\text{La}_{0.18}\text{Sr}_{0.82}\text{Al}_{0.59}\text{Ta}_{0.41}\text{O}_3(001)$ (LSAT) single crystals in order to study the role of the interface, strain, and doping on the magnetic and transport properties. We find that while increased doping favors antiferromagnetic ordering, strain is the driving mechanism for the change in the magnetic properties. X-ray spectroscopy shows a direct link between strain and orbital occupancy, which ultimately determines the electronic and magnetic properties of the strained LSMO films through the competing antiferromagnetic superexchange and ferromagnetic double exchange interactions.

Both SrTiO_3 and LSAT are cubic perovskites at room temperature, with lattice parameters of 3.905 and 3.868 Å, respectively [31,32]. The bulk crystal structure of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ at $x = 0.45, 0.50$, and 0.55 has been investigated by Chmaissem *et al.* [30]. For $x = 0.45$, LSMO is ferromagnetic and crystallizes in a rhombohedral ($R3c$) crystal structure, with $a = b = 5.47598$ Å, $c = 13.3461$ Å, and $\gamma = 120^\circ$ (300 K). For

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$x = 0.50$ and 0.55 , LSMO has a high-temperature tetragonal ($I4/mcm$) structure (ferromagnetic), with $a = 5.444\,61\text{ \AA}$, $c = 7.759\,5\text{ \AA}$ ($x = 0.50$) and $a = 5.433\,78\text{ \AA}$, $c = 7.745\,5\text{ \AA}$ ($x = 0.55$) at 300 K , while at low temperatures it becomes orthorhombic ($Fmmm$) with A-type antiferromagnetic ordering. In terms of a pseudocubic lattice parameter, $a_{pc} = a/\sqrt{2}$, we obtain $a_{pc} \approx 3.87\text{ \AA}$ ($x = 0.45$), $3.85\text{ \AA}$ ($x = 0.50$), and $3.84\text{ \AA}$ ($x = 0.55$). Hence, the LSAT substrate is nearly lattice matched with LSMO for Sr dopings near 0.5 , while SrTiO_3 has a negative lattice misfit up to -1.7% .

II. SAMPLE GROWTH AND EXPERIMENTAL METHODS

The samples investigated in this study consist of 15 unit cell (u.c.) $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films with $x = 0.47$, 0.50 , and 0.55 , grown on TiO_2 -terminated $\text{SrTiO}_3(001)$ and LSAT(001) single-crystal substrates by molecular beam epitaxy in an ultrahigh vacuum system with a base pressure of 1×10^{-10} mbar. As a reference, a 75-u.c.-thick $\text{La}_{0.53}\text{Sr}_{0.47}\text{MnO}_3$ film was also deposited on TiO_2 -terminated $\text{SrTiO}_3(001)$. The LSMO films are deposited by coevaporation of the elemental metals from individual effusion cells, with the individual evaporation rates determined to within 2% by a calibrated quartz crystal thickness monitor, under an oxygen partial pressure of 1×10^{-7} mbar (feedback controlled by a mass spectrometer). The substrates are held at 720°C and are cooled to room temperature after growth under the same oxygen environment as during growth, following the same growth procedure as described in Ref. [33]. The surface crystallinity and film orientation are monitored during growth using reflection high-energy electron diffraction (RHEED). The diffraction patterns show that the films are $[001]$ -oriented and coherently strained to the SrTiO_3 and LSAT substrates. The RHEED patterns exhibit sharp spots lying on a Laue arc, characteristic of atomically smooth surfaces, as shown in Fig. 1; oscillations in the intensity of the RHEED diffraction spots (used to monitor the LSMO film thickness), with a period coincident with the completion of each layer, indicate that the film growth proceeds in a layer-by-layer fashion. The LSMO films with $x = 0.47$ and 0.50 grown on SrTiO_3 additionally show a $c(2 \times 2)$ surface reconstruction. The observation of such reconstruction in LSMO films has been reported before [33,34]. This reconstruction could be the result of a true surface reconstruction, common in perovskite surfaces, although we attribute it to the lower crystal symmetry of the rhombohedral LSMO [35]. In fact, the onset at small thicknesses of long-ranged twinning in LSMO films associated with a coherent rotation of the oxygen octahedra has been well documented [36–41]. With the exception of the 15-u.c. $\text{La}_{0.53}\text{Sr}_{0.47}\text{MnO}_3/\text{SrTiO}_3(001)$ sample, the LSMO films are annealed *ex situ* at 600°C for 6 h in flowing O_2 after deposition prior to magnetic, transport, and x-ray spectroscopic characterization.

The magnetotransport properties of the LSMO films as a function of temperature and magnetic field are measured in a van der Pauw configuration, with the resistivities being corrected by a corresponding geometrical factor of $\pi/\ln(2)$ [42]. Bulk magnetic properties are measured by superconducting

FIG. 1. RHEED patterns of the LSMO films grown on $\text{SrTiO}_3(001)$ and LSAT(001) along the $\langle 100 \rangle$ azimuth, after film deposition. The incident electron energy is 15 keV .

interference device (SQUID) magnetometry, with the magnetic field applied in-plane along the $\langle 100 \rangle$ azimuth.

X-ray absorption spectroscopy (XAS) measurements were carried out at beamline U4B of the National Synchrotron Light Source at Brookhaven National Laboratory. The spectra are acquired in the total electron yield mode, using circular (70% polarization) and linearly (100%) polarized light; measurements of both the incident light intensity and of a NiO reference sample are acquired simultaneously for intensity normalization and as an energy reference, respectively. In the Ni L -edge energy region, one also measures the La M_4 edge of the LSMO films, which we also use to confirm the energy calibration. To probe the magnetic moment, we use the x-ray magnetic circular dichroism (XMCD) effect, which corresponds to the difference in absorption for left and right circularly polarized light in a magnetic system [43–45]. For the measurements reported here, the light polarization is fixed and the x-ray absorption spectra are measured for the two directions of the sample magnetization, with the sample plane set parallel to the applied magnetic field and at 45° with respect to the x-ray beam. Before each spectrum is measured, the sample is set in a uniform magnetic state by applying a field pulse of $\pm 450\text{ Oe}$, while a holding field of $\pm 120\text{ Oe}$ is present during the measurements to prevent depolarization. The x-ray slit settings used in these measurements limit the energy resolution to about 0.53 eV over the Mn L edge. The absorption spectra are processed by subtracting a linear background and normalized by setting the preedge intensity to zero and the postedge intensity to unity, but otherwise are not corrected for the degree of polarization nor for the angle of measurement, which amounts to a simple scaling factor in the XMCD signal, common to all spectra. One advantage of magnetic x-ray absorption spectroscopy lies in the fact that, by tuning the x-ray energy to the absorption edge of

Mn (which is responsible for the magnetic polarization), the magnetic moment of the sample can be measured independent of other spurious contributions, such as magnetic impurities that may be present in the substrate. The probing depth of XMCD measured in the total electron yield mode is also small, on the order of a few nanometers, mostly determined by the escape depth of excited secondary electrons [46]. Measurements with linearly polarized light at both the Mn $L_{2,3}$ and O K edges (500–680 eV) are carried out to probe the LSMO in-plane and out-of-plane orbital states. An asymmetry in the orbital occupancy is expected both from the symmetry breaking introduced by the interface and by the presence of biaxial strain, which imposes a tetragonal symmetry on the system. The measurements are carried out at room temperature under no magnetic field, with the sample normal parallel to the x-ray beam for the in-plane (IP) measurements (electric field oscillating in the plane of the film, along the $\langle 100 \rangle$ azimuth) and with the sample normal at 60° to the x-ray beam, giving a dominant out of plane (OOP) electric field component. The energy resolution for these measurements is ~ 0.18 eV at the O K -edge and ~ 0.27 eV at the Mn L -edge energies.

III. RESULTS AND DISCUSSION

The temperature variation of the resistivity of the LSMO films at 0 and 50 kOe are presented in Fig. 2 (full and dashed lines, respectively). The resistivities found for these thin films are higher than for the corresponding bulk values, but within the same order of magnitude [29]. The resistivity behavior can be divided into three distinct regimes: a high-temperature insulating regime (i.e., with a negative temperature rate of variation), an intermediate metallic regime (with positive temperature rate of variation), and a low-temperature insulating regime. All samples exhibit a resistivity maximum between the high- and intermediate-temperature regimes, which in the CMR manganites is closely related to the magnetic critical temperature [19,47]. The films grown on SrTiO₃ tend to be more conducting than those grown on LSAT for the same Sr content. The resistivity decreases with increasing doping, although this behavior is reversed for the $x = 0.50$ and $x = 0.55$ films grown on LSAT. The effect of the applied magnetic field is that of decreasing the resistivity, consistent with the double exchange mechanism and the CMR effect operative in these compounds. However, the magnitude of the magnetoresistance varies greatly across the samples, being very large for the films grown on LSAT and for the 0.47 doping on SrTiO₃, and very small for the 0.50 and 0.55 dopings on SrTiO₃, as shown in Figs. 2(d) and 2(e). Also common to most films (the exception is $x = 0.50$ on LSAT) is an increase in resistivity below about 50–100 K, marking the onset of an insulating state associated with a very large negative magnetoresistance effect of up to 50% for the case of 0.47 doping on SrTiO₃[48]. The resistivity curves for the LSMO films grown on SrTiO₃ exhibit a cusp at around 105 K, which is the temperature corresponding to the cubic-to-tetragonal transition of SrTiO₃; the cusp in the resistivity can be better visualized as a sudden jump in the temperature derivative, as shown in Fig. 2(c). The change is more pronounced for 0.47 Sr doping. This strong modification in the transport properties is attributed to a resonant phonon coupling between the substrate

FIG. 2. (Color online) (a,b) Variation of the resistivity versus temperature for LSMO films grown on SrTiO₃ and LSAT, respectively. (c) Variation of the temperature derivative of the resistivity for the LSMO films grown on SrTiO₃ near the cubic to tetragonal phase transition of SrTiO₃. (d,e) Temperature (T) dependence of the magnetoresistance, $\Delta\rho/\rho = (\rho_{50} - \rho_0)/\rho_0$, versus temperature for the LSMO films grown on SrTiO₃ and LSAT, respectively. Full and dashed lines correspond to measurements at zero (ρ_0) and 50 kOe (ρ_{50}) applied magnetic field, respectively. The Sr dopings are as labeled.

and the LSMO film which leads to enhanced electron-phonon scattering at the interface between LSMO and SrTiO₃ [25].

The variation of the magnetization as a function of temperature (at 500 Oe) and magnetic field (at 100 K) is shown in Figs. 3(a) and 3(b), respectively, where the linear diamagnetic contribution of the substrate is removed from the data, except for the LSAT contribution in the M - T curves. We find that for two samples (0.47 and 0.55 grown on SrTiO₃), a strong constant magnetic component is present from 300 to 350 K, suggesting that the samples are magnetic up to much higher temperatures; such a magnetic component is also observed in the M - H loops. However, since the x-ray magnetic spectroscopy measurements at room temperature at the Mn L edge in these samples show no circular dichroism, we attribute this small ferromagnetic component to magnetic impurities

FIG. 3. (Color online) Magnetic response of the LSMO films as a function of (a) temperature (in a 500-Oe field) and (b) magnetic field (at 100 K). (c) X-ray magnetic circular dichroism spectra for the LSMO films at different dopings grown on LSAT and SrTiO₃ (at $T = 80$ K). Spectra have been shifted vertically for ease of display. (d) Diagram showing the magnetic state of the LSMO films as a function of lattice misfit and doping. The inset shows the variation of the magnetic moment (μ) with lattice mismatch (ϵ) of the LSMO films. (Circles correspond to LSMO grown on LSAT, triangles to LSMO grown on SrTiO₃.)

unrelated to the LSMO film [49,50]; hence, we have omitted the corresponding M - H curves from Fig. 3(b).

The change in the magnetic properties both as a function of doping and substrate are striking; for the samples grown on SrTiO₃, only the 0.47 doping develops a ferromagnetic component, while the 0.47 and 0.50 samples grown on LSAT show the strongest ferromagnetic response. In all cases, the low-temperature saturation moment is strongly reduced as compared to the expected nominal bulk value of about $3.5 \mu_B/\text{Mn}$, but in agreement with the reduced values found for bulk LSMO at half doping. In fact, for the 0.50 doping on LSAT, the saturation magnetic moment is close to that of the bulk, about $2 \mu_B/\text{Mn}$ [29]. The observation of reduced magnetic moments in LSMO in this doping range has been attributed to the presence of antiferromagnetic phases (phase separation) or due to spin canting, while in thin films one often observes reduced interfacial moments induced by nonuniform chemical profiles [13–15,51–54]. However, the magnetization increases monotonically with decreasing temperature, in contrast to the bulk behavior, where abrupt drops in the magnetization with decreasing temperature indicate the sudden onset of a low-temperature antiferromagnetic state [26,29]. The strong depression of the magnetic moment observed at around 100 K for the $x = 0.47$ LSMO films grown on SrTiO₃, coincident with an enhanced resistivity, is attributed to a resonant phonon coupling between

the substrate and the LSMO film which leads to enhanced magnon-phonon scattering and a resulting reduction in the saturation magnetization [25].

The onset of magnetism observed in the magnetometry data correlates well with the position of the resistivity peak in the resistivity versus temperature curves shown in Fig. 2. The samples that exhibit nearly no magnetic response (0.50 and 0.55 grown on SrTiO₃ and 0.55 grown on LSAT) have pronounced temperature resistivity peaks, which we attribute to the onset of metallic antiferromagnetic order in the system [26]. This conclusion is in agreement with the results of Santos *et al.* [48], who observe the presence of antiferromagnetic order in ca. 30 nm LSMO films grown on SrTiO₃(001) using neutron diffraction measurements at $x = 0.5$ and 0.55 dopings. Our data therefore suggest that, for a given substrate, higher Sr doping favors antiferromagnetic ordering but that the absolute doping value is not sufficient to determine the magnetic order. The XMCD spectra for the different samples, measured at 80 K, are presented in Fig. 3(c). The XMCD data largely confirm the bulk magnetometry results, showing a close correspondence between the magnetic moment measured by SQUID and the amplitude of the dichroic signal. The LSMO film at 0.50 doping grown on LSAT shows the strongest ferromagnetic component, while the 0.50 sample grown on SrTiO₃ displays no measurable dichroism, to within the noise level; for the 0.55 doped sample grown on LSAT a very small magnetic component is detected, in agreement with the SQUID data. We find no magnetic dichroism at room temperature for the 0.55 and 0.47 doped samples grown on SrTiO₃, indicating that the constant magnetic signal measured in the M - T curves [Fig. 2(a)] does not originate from exchange interactions between the Mn cations in the LSMO films.

Comparing the magnetoresistance response [Figs. 2(e) and 2(f)] with the magnetometry results shows that the magnetoresistance is smallest for the LSMO films exhibiting antiferromagnetic order (films with 0.50 and 0.55 dopings grown on SrTiO₃); in particular, no enhancement of the magnetoresistance at the onset of magnetic order is observed for these samples, in contrast to the samples where a ferromagnetic component is measured. For example, the LSMO film with 0.55 doping grown on LSAT, where a nearly vanishing ferromagnetic component is seen to develop at around 200 K, shows a very large magnetoresistance that peaks at about -40% around the same temperature. The fact that the observed magnetoresistance amplitude is characteristic of the CMR effect and that the response is larger the less homogeneous the magnetic state of the system is (as measured by the presence of a magnetic moment much smaller than the saturation value) suggests the presence of phase separation in such films [55]. However, the upturn in the resistivity with decreasing temperature observed at low temperatures for most samples seems to be an unrelated phenomenon, since we do not observe a decrease in the magnetisation in the low-temperature regime that would accompany such a process. In addition, the most strongly ferromagnetic sample (0.50 doping on LSAT) shows no increase in resistivity with lowering temperature, suggesting that the ferromagnetic phase remains metallic. This fact points to the presence of a charge localization process that affects the antiferromagnetic component of the system, either related to disorder-induced localization or to charge ordering.

FIG. 4. (a) X-ray absorption spectra for the different LSMO films using linearly polarized light with the electric field oscillating along the in-plane (IP) $\langle 100 \rangle$ azimuth (full lines) and out-of-plane (OOP) direction (dotted lines). (b) The corresponding linear dichroism (out-of-plane minus in-plane XAS spectra). For ease of display, the spectra have been shifted vertically (ordered by increasing lattice misfit) and the plotted data for the XAS O K edge have been multiplied by a factor of 2.

As mentioned above, the lattice constant of LSMO changes with Sr doping content, and one therefore expects that the different LSMO films will be differently strained when grown on the same substrate. Indeed, when one considers the misfit strain (which is the negative of the lattice misfit, in the definition used here), one finds a striking correlation with the magnetic state: the less strained films have a large ferromagnetic component, while the strongly tensile strained films are predominantly antiferromagnetic. This correspondence can be seen clearly when plotting the magnetic moment with film misfit strain [Fig. 3(d), inset]. A phase diagram of the magnetic state versus strain and doping [Fig. 3(d)] reveals a sharp transition between ferromagnetic and antiferromagnetic states at a lattice misfit of about -1.0% .

To understand the link between the magnetic and lattice properties, we turn to the results of the linearly polarized x-ray absorption measurements, shown in Fig. 4, where we subtract a linear background contribution (using the O K preedge data points) and normalize by setting the intensity at the Mn preedge to unity. At room temperature the LSMO films are nonmagnetic, and the linear dichroism probes only the electronic degrees of freedom (natural linear dichroism). The spectra are ordered by increasing misfit strain; we have omitted the higher-energy portion of the O K edge, which is dominated by hybridized Sr and La states [56]. The overall shape of the absorption spectra is similar to that reported in the literature for LSMO, both at the O K and Mn $L_{2,3}$ edges [56,57]. In particular, the spectra for 15 u.c. LSMO/SrTiO₃(001) (0.47 doping) is similar to that of the 75 u.c. LSMO/SrTiO₃(001) film, except for slightly less pronounced absorption peaks at around 533 eV at the O K edge. From the averaged (unpolarized) XAS spectra (not shown), one finds a shift in

the energy position of the Mn L_2 peak with Sr doping of 0.2 eV between $x = 0.47$ and 0.55 , independent of strain. Such a shift in the energy peak position with doping is in qualitative agreement with the results of Abbate *et al.*, who observe a total change in the peak position of 1 eV over the La_{1-x}Sr_xMnO₃ series [56], an effect that can be explained in terms of a chemical shift, where an increase in valence leads to a lowering in the energy of the core levels, requiring higher photon energies for excitation [56,58].

At the O K edge, the preedge features in the energy range from 529 to 535 eV have been assigned to transitions from the O $1s$ to empty O $2p$ states, where the latter arise as a consequence of hybridization of the O $2p$ with the Mn $3d$ orbitals [57,59–61]. It is suggested that these transitions offer a more direct projection of the cationic density of states (DOS) as compared to the $L_{2,3}$ transitions due to the smaller role of core hole effects (*excitons*) on the cation DOS at the oxygen site [61]. In particular, the energy peaks in the range from 530 to 535 eV have been assigned to transitions into the partially filled $e_g \uparrow$ band and to the empty $t_{2g} \downarrow$ and $e_g \downarrow$ states [56,57,62]. In our case, we find that the first two peaks are composed of two components, separated by about 0.7 eV for the lower energy peak at around 531 eV and about 1.0 eV for the peak lying at around 533.5 eV. Although the O K -edge absorption spectra of the mixed valence manganites do not correspond to a simple superposition of the spectra of the pure cationic states (Mn³⁺ and Mn⁴⁺) due to a high degree of covalency, one may understand such fine structure as arising from the energy splitting in the high-symmetry e_g and t_{2g} bands of the Mn³⁺ and Mn⁴⁺ cations due to the tetragonal distortion induced by strain, as shown schematically in Fig. 5 from the ⁵D ground-state configuration of $3d^3$ electrons in an octahedral

FIG. 5. Schematic diagram of the energy levels in Mn^{3+} in an octahedral crystal field (in cubic and tetragonal symmetries). Upward-pointing arrows represent occupied spin-up states. $10D_q$ is the crystal field splitting, and $\delta = 4D_s + 5D_t$, $\zeta = 3D_s - 5D_t$ are the energy splittings introduced by the tetragonal distortion (where D_s , D_t are energy-splitting parameters).

crystal field. The ground state of Mn^{4+} is a 4F configuration, but one may expect only slight changes in the electronic energies when removing one electron from a 5D state such that the electronic arrangement of the 4F state ought to resemble closely that of a 5D configuration [63,64]. This is corroborated by estimating the energy difference between such features for the line at 531 eV as a function of lattice misfit, plotted in Fig. 6, which shows that the energy separation increases steadily with increasing misfit strain for both in-plane and out-of-plane polarization measurements. One also observes an abrupt change in the energy separation between the two peaks for the out-of-plane polarization for the LSMO films grown on SrTiO_3 as compared to LSAT, suggesting an interfacial contribution to the out-of-plane orbitals in addition to strain in the former case.

One striking feature in the O K -edge spectra is a systematic shift towards higher energies of the out-of-plane polarized absorption spectra with respect to the in-plane spectra with

FIG. 6. Variation of the low-energy absorption peak separation as a function of lattice mismatch. The asterisk (*) denotes data points for the 75-u.c. LSMO film. Dashed lines are guides to the eye.

increasing misfit strain. At the Mn L edge, the relative position of the spectra shows a similar trend, although the effect is more subtle. For the in-plane x-ray absorption spectra, the electric field lies in the plane of the sample, along the $\langle 100 \rangle$ azimuth, and therefore probes the $x^2 - y^2$ orbitals, while for the out-of-plane spectra, the electric field probes mostly the $3z^2 - r^2$ orbitals [65]. The shift of the out-of-plane spectra to higher energies with increasing tensile strain can then be interpreted as a shift to higher energies of the $3z^2 - r^2$ orbital states, in agreement with the expectation that the $x^2 - y^2$ orbital occupancy is favored for tensile strain [27,57]. A better visualization of the changes in the occupancy of the valence states can be gathered by plotting the linear dichroism, shown in Fig. 4(b), as the difference between the out-of-plane and in-plane absorption spectra. The t_{2g} orbitals point in directions away from the electric field direction and should therefore have a weak polarization dependence, such that the contribution from these orbitals is expected to largely cancel out in the linear dichroism plot [65]. Again, for the O K edge, the variation in the linear dichroism is strong and includes a marked change in shape in the energy range from 529 to 532 eV, associated with transitions into empty $e_g \uparrow$ states. Two main features are noticeable, at 530.1 and 530.85 eV, which are seen to change markedly in amplitude and sign with varying misfit strain. The feature at 530.1 eV, associated with the leading edge of the absorption spectra, shows a change in sign between 0.90% and 1.43% misfit strain and is consistent with a relative shift towards higher energies of the out-of-plane states with increasing misfit strain, or conversely, a favoring of in-plane orbitals with increasing strain. The feature at 530.85 eV sits at the leading edge of the second peak and shows the opposite trend as the feature at 530.1 eV; a similar interpretation implies a favoring of out-of-plane orbitals at the second absorption peak, which agrees with the assignment of these features to the strain-split $e_g \uparrow$ states (cf. Fig. 5). Hence, the effect of strain is to gradually modify the in-plane and out-of-plane orbital occupancy, manifested in a change in the sign of the linear dichroism at the O K edge (530.1 eV). A similar difference in the sign of the linear dichroism has been observed in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films grown under large tensile (on SrTiO_3) and compressive (on LaAlO_3) strains [57]. Tensile strain leads to a decreased Mn-O bond length along the out-of-plane direction, while the opposite occurs for compressive strain [57]. Such changes in orbital occupancy and orbital overlap are expected to lead to strong modifications in the magnetic exchange interactions and in the magnetic properties of the system. In the CMR manganites, the magnetic properties are predominantly determined by competing superexchange (mediated by the localized t_{2g} electrons) and double-exchange interactions (mediated by the itinerant e_g electrons). An increase in the in-plane orbital overlap due to a reduction in the in-plane Mn-O bond length is expected to enhance electron hopping in-plane, favoring the ferromagnetic double-exchange interaction and in-plane ferromagnetic coupling of the spins. If this is accompanied by a weakened electron hopping along the out-of-plane direction, then one may expect a superexchange-driven antiferromagnetic coupling between successive spin planes, and the resulting spin configuration corresponds to A-type antiferromagnetic order in strongly tensile strained LSMO films. The converse effect leads

to enhanced ferromagnetic coupling along the out-of-plane direction and an antiferromagnetic coupling within the plane which corresponds to C-type antiferromagnetic ordering at large compressive strains [27]. At intermediate strains the orbital overlap is expected to be more uniform, favoring ferromagnetic order. Our results indicate an abrupt transition between ferromagnetism to antiferromagnetism at a lattice misfit of about -1% , while the reduced saturation moments and the very large magnetoresistance effects characteristic of CMR at around that strain value suggest the presence of a mixed phase system, with competing ferromagnetic and A-type antiferromagnetic phases.

IV. CONCLUSIONS

In conclusion, we have carried out a detailed magnetic and spectroscopic characterization of thin LSMO films at near half doping, both as a function of doping and misfit strain. We find that the magnetic and transport properties depend sensitively on the film strain: antiferromagnetic configurations are favored at higher tensile strains, while a strong ferromagnetic

component develops at tensile strains below about 1% and becomes dominant for near-zero misfit strains. In the intermediate strain region, one infers the coexistence of both phases; the magnetoresistance of such films tends to be largest, up to -50% near the magnetic critical temperature. The x-ray spectroscopic characterization shows that, with increasing tensile strain, the $x^2 - y^2$ orbitals of the e_g manifold become increasingly more populated; this is seen as a change in sign of the linear dichroism at around -1% lattice misfit. These changes in orbital occupancy lead to changes in the magnetic ground state, from ferromagnetic at small tensile strains to antiferromagnetic at large tensile strains.

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