Doping dependent electronic and magnetic ordering in mixed-valent La$_{1-x}$Sr$_x$MnO$_3$ thin films

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Abstract

We have investigated the collective electronic and magnetic orderings of a series of La$_{1-x}$Sr$_x$MnO$_3$ thin films grown epitaxially strained to (001) oriented strontium titanate substrates as a function of doping, $x$, for $0 \leq x \leq 0.4$. We find that the ground states of these crystalline thin films are, in general, consistent with that observed in bulk crystals and thin film samples synthesized under a multitude of techniques. Our systematic study, however, reveal subtle features in the temperature dependent electronic transport and magnetization measurements, which presumably arise due to Jahn-Teller type distortions in the lattice for particular doping levels. For the parent compound LaMnO$_3$ ($x = 0$), we report evidence of a strain-induced ferromagnetic ordering in contrast to the antiferromagnetic ground state found in bulk crystals.

1. Introduction

The mixed valent manganites are an interesting class of materials due to their strongly correlated electronic and magnetic orderings [1, 2]. In this study, we focus on La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) crystalline thin films grown in the perovskite ABO$_3$ crystal structure where the La and Sr atoms occupy the A-site and the Mn atoms occupy the B-site. The dependence of the electronic and magnetic orderings on doping given by $x$, the ratio of Sr/(La+Sr), has been studied in bulk single crystals [3–6]. Furthermore, in both bulk and thin film form the colossal magnetoresistive (CMR) effect in this material around $x = 0.3$ doping has also been studied extensively over the past three decades [1, 2, 7]. In thin film form, the studies around $x = 0.3$ doping have also included probing the use of epitaxial strain imparted by a substrate [8–10] and the synthesis of atomically ordered superlattice structures [11–13] to control and manipulate the magnetic order. Here we conduct a systematic study probing the electronic and magnetic orderings in a series of identically prepared thin films as a function of doping $x$.

In the parent compound LaMnO$_3$ ($x = 0$), the electron configuration of Mn$^{3+}$ is 3$d^3$; $t^3_2$ $e^1_2$, and due to ordering of the $e_g$ orbitals, cooperative Jahn-Teller distortions arise [2]. By substituting some La$^{3+}$ with Sr$^{2+}$, Mn$^{4+}$ is created and holes are introduced in the $e_g$ band corresponding to $x$, the amount of Sr content. At 0.17 < $x$ < 0.5 the resulting materials are typically conducting ferromagnets [1, 2]; the mobile $e_g$ electrons mediate a ferromagnetic interaction between neighboring Mn$^{3+}$ and Mn$^{4+}$ sites, which is known as the double exchange interaction.

LSMO films around $x = 0.3$ doping have also been explored for potential device applications like magnetic tunnel junctions and spin valves [14–16], given that the double exchange interaction suggests a nearly spin polarized half metal [14, 15, 17]. Here we systematically explore the doping dependence of correlated electronic and magnetic orderings in strained epitaxial thin films of La$_{1-x}$Sr$_x$MnO$_3$.

2. Experimental details

The samples used in this study were grown using ozone-assisted Molecular Beam Epitaxy (MBE) [18]. By this method, LSMO films were grown one molecular layer (ML) at a time, with dopings of $x = 0.00, 0.04, 0.17, 0.20, 0.33$...
and 0.40, on (001) oriented strontium titanate (STO) substrates at a growth temperature of ~700 °C. The substrates were etched with dilute HCl prior to growth to obtain a TiO\textsubscript{2} terminated surface, which provided a consistent starting template for the growth of each film studied here. Reflection High-Energy Electron Diffraction (RHEED) was used throughout each film growth to monitor the samples, which indicated that the films were epitaxially strained to the

Figure 1. Representative RHEED images obtained during the growth of the \(x = 0.40\) sample illustrate the crystal quality of the film. (a) TiO\textsubscript{2} terminate substrate STO surface, (b) after 5 ML LSMO surface, (c) after 130 ML LSMO surface, (d) LSMO surface at the end of film growth (250 ML).

Figure 2. Electronic transport and magnetization measurements for a representative \(x = 0.33\) sample. (a) Resistivity versus temperature measurements. As the temperature is decreased an insulator to metal transition is observed ~340 K. (b) Magnetization versus temperature measurements made in a 0.0100 T field (black). As the temperature is decreased an onset from a paramagnetic to a ferromagnetic transition occurs ~350 K. The low temperature fit (green) indicates an \(M_{\text{Sat}} \sim 3.7 \mu_\text{B}/\text{Mn}\).
Figure 3. Magnetic hysteresis measured for $x = 0.33$ doping at 5 K. The line is a guide to the eye.

Figure 4. Electronic transport and magnetization measurements for an $x = 0.40$ sample. (a) Resistivity versus temperature measurements. As the temperature is decreased a gradual change is observed from a 'bad metal' at high temperatures to a 'better metal' at low temperatures. (b) Magnetization versus temperature measurements made in a 0.0100 T field (black). As the temperature is decreased an onset from a paramagnetic to a ferromagnetic transition occurs $\sim 325$ K. The low temperature fit (green) indicates an $M_{\text{sat}} \sim 1.9 \mu_B/\text{Mn}$. 
substrate with excellent crystal quality. Figure 1 shows representative RHEED images taken in situ during the growth of the \( x = 0.40 \) sample. The starting TiO\(_2\) terminated STO surface is shown in figure 1(a) while figures 1(b), (c) and (d) show diffraction patterns from the LSMO film surface at different stages of the growth: after 5 ML, after 130 ML, and at the end of growth (250 ML), respectively. The other samples studied also showed similar RHEED patterns, indicating excellent crystalline quality.

Distilled ozone was used as the oxidation source and an ozone partial pressure of \( 5 \times 10^{-7} \) torr was maintained in the chamber throughout each growth. The La, Sr and Mn source fluxes were adjusted to obtain a growth rate of \( \sim 30 \) s/ML and were flux matched to within \( \sim 5\% \) based on the desired stoichiometry. Each ML was grown by pseudo-codeposition of the La, Sr and Mn atoms—i.e. while the elements were deposited together, the source shutters were individually activated to account for the \( \sim 5\% \) variation in flux matching, thereby depositing exactly the required stoichiometric ratio of atoms for each ML. The series of samples with different doping studied here were all grown to a thickness of \( \sim 1000 \) Å.

Resistivity of these thin films as a function of temperature were obtained from resistance measurements made using a modified Van der Pauw method [19]. This four point measurement scheme, where current was sourced through two contacts and the voltage was measured through two other contacts eliminated contact resistances factoring into the measurements and provided accurate measurements of film resistance. The measurements were made using a dip probe that allowed the sample temperature to be varied from as high as \( \sim 380 \) K down to liquid helium temperatures.

Magnetization measurements on the La\(_{1-x}\)Sr\(_x\)MnO\(_3\) samples were conducted at temperatures between 2 and 400 K and in fields up to 7 T. Measurements were made using a Quantum Design XL7 superconducting quantum interference device (SQUID) magnetometer with the field parallel to the film surface. The diamagnetic signal due to the substrate was subtracted.

3. Experimental results and discussion

To probe the electronic and magnetic ordering in these samples as a function of doping, we use the resistivity and magnetization measurements described above. Given that La\(_{1-x}\)Sr\(_x\)MnO\(_3\) samples with doping \( x \sim 0.3 \) has been
Extensively studied, we begin by probing the $x=0.33$ sample. As observed in single crystals [1, 3, 5–7] and thin films [7, 8, 11, 12], we find the ground state is metallic and ferromagnetic.

Resistivity as a function of temperature was studied on many films with the $x=0.33$ doping. Here we present data from a representative sample for which we have measured both resistivity and magnetization. The electronic transport measurements (figure 2(a)) show a local maximum in the resistivity $\sim 340$ K indicating an insulator-to-metal transition that occurs at $\sim 340$ K as the temperature is lowered. The residual resistivity (at 4.2 K) of the ground state of this sample is $\sim 500 \mu \Omega$-cm with a residual resistivity ratio (RRR) measured from 300 to 4.2 K of $\sim 21$. In understanding this data, it is important to note that the MBE films were not rotated during deposition. The fixed orientation of each elemental source resulted in a small gradient of each elemental flux over the sample surface and therefore, small stoichiometric variations in the A:B ratio. The use of ozone as the source of oxygen, we believe fully oxygenates the samples. But, the B:O ratio assumed to be 1:3 has not been measured. Conservatively, we estimate that both the A:B ratio and the B:O ratio have an uncertainty of $\sim \pm 5\%$. This is consistent with the electronic transport measurements we have observed in a large number of samples at $x \sim 0.3$ doping where we have observed the highest $T_c$ values, as high as 370 K, and the lowest residual resistivity values, as low as 40 $\mu \Omega$-cm.

The magnetization as a function of temperature measured in a 0.0100 T field (figure 2(b)) indicates a transition to a ferromagnetic phase with an onset temperature (where the magnetization deviates from zero), $T_{\text{onset}}$ of around 350 K. Note the $\sim 60$ K range below $T_{\text{onset}}$ where the shape of the magnetization profile deviates from that of a smooth 2nd order phase transition. This high temperature ‘foot’ is likely due to the small variations in stoichiometry (A:B and B:O ratios) across the sample as discussed above. As the sample temperature is reduced, the magnetization increases and approaches a saturation value at low temperatures. A fit to the low temperature data is also shown as a line in figure 2(b), which was obtained using the theoretical model

$$M = M_{\text{Sat}}(1 - a_1 T^{3/2}),$$

where $M_{\text{Sat}}$ is the saturated value of the magnetization and the $a_1 T^{3/2}$ term is the standard term due to spin density waves according to the Block $T^{3/2}$ Law [20]. The data and the fit indicates an $M_{\text{Sat}}$ value of $\sim 3.7 \mu \text{B}/\text{Mn}$. 

Figure 6. Electronic transport and magnetization measurements for a $x = 0.17$ sample. (a) Resistivity versus temperature measurements. As the temperature is decreased an insulator-to-metal transition is observed $\sim 210$ K followed by a re-entrant metal-to-insulator transition $\sim 170$ K, which leads to an insulating ground state. (b) Magnetization versus temperature measurements made in a 0.0100 T field (black). As the temperature is decreased an onset from a paramagnetic to a ferromagnetic transition occurs $\sim 230$ K. The low temperature fit (green) indicates an $M_{\text{Sat}} \sim 1.7 \mu \text{B}/\text{Mn}$. 

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This measured $M_{\text{Sat}}$ value is consistent with what is expected for the $x = 0.33$ sample based on the double exchange interaction assuming a nearly 100% spin polarization \cite{14, 15}.

Figure 3 shows a magnetization versus field measurement made at 5 K. The observed hysteresis loop is characteristic of the ferromagnetic ground state at this $x = 0.33$ doping. The value of the coercive field at 5K, $H_c = 0.0061$ T, was determined by a linear coercive field fit using data points above and below the field axis to find the intercept with that axis. This measured $H_c$ is consistent with what has been observed in bulk and thin film samples \cite{21–23}.

Similar to the $x = 0.33$ doping, the $x = 0.40$ sample shows a ground state that is metallic and ferromagnetic. In contrast to the $x = 0.33$ sample, the electronic transport measurements (figure 4(a)) for the $x = 0.40$ sample, however, does not show an insulator-to-metal transition but rather a gradual change from a 'bad metal' at high temperatures to a better metal at low temperatures. It is useful to note that such a 'bad metal' at high temperatures (where the sample is paramagnetic) to a metal at low temperatures (where the sample is ferromagnetic) is also observed for bulk crystals \cite{3, 5}. Due to the epitaxial strain imparted by the substrate, the doping $x$ at which this 'bad metal' to metal transition is observed in our thin films could be different to that of the bulk crystals. The residual resistivity (at 4.2K) of the ground state of our $x = 0.40$ thin film sample is $\sim 13000$ $\mu\Omega$-cm, which in comparison to our $x = 0.33$ sample is more than a factor of 25 larger while the residual resistivity ratio (RRR) measured from 300 to 4.2 K of $\sim 20$ is similar to that of the $x = 0.33$ sample.

The magnetization as a function of temperature for this sample (see figure 4(b)) also shows a transition to a ferromagnetic phase with an onset temperature, $T_{\text{onset}}$, around 325 K and a foot that extends about 70K below $T_{\text{onset}}$ where the shape of the magnetization profile deviates from that of a smooth 2nd order phase transition. Again this high temperature ‘foot’ is likely due to the small variations in stoichiometry (A:B and B:O ratios) across the sample as previously discussed. The fit to the low temperature magnetization data indicates a saturation magnetization $M_{\text{Sat}}$ of $\sim 1.9$ $\mu_B$/Mn, which is significantly reduced from the saturation magnetization of $\sim 3.7$ $\mu_B$/Mn found for the $x = 0.33$ sample. The coercive field of $H_c = 0.0080$ T extracted from magnetization versus field measurements made at 5 K for the $x = 0.40$ sample is comparable to that observed for the $x = 0.33$ sample.

Figure 7. Electronic transport and magnetization measurements for a $x = 0.04$ sample. (a) Resistivity versus temperature measurements. As the temperature is decreased the sample remains in an insulating state. (b) Magnetization versus temperature measurements made in a 0.0100 T field (black). As the temperature is decreased an onset to a state with canted antiferromagnetically aligned spins is observed $\sim 155$ K. The low temperature fit (green) indicates a very small $M_{\text{Sat}}$ value $\sim 0.3$ $\mu_B$/Mn. The inset shows a zoomed in view of the low temperature magnetization and points to a sudden change in the magnetization $\sim 43$ K.
Changing the doping in the opposite direction—decreasing [Sr] from $x = 0.33$ as opposed to increasing [Sr]—we again find a metallic and ferromagnetic ground state for the $x = 0.20$ sample. Electronic transport measurements, (figure 5(a)), in this case reveal a somewhat sharper insulator-to-metal transition as a function of temperature than for doping $x = 0.33$. This high temperature insulator to low temperature metal transition for the $x = 0.20$ sample occurs $\sim 300$ K, a lower transition temperature than for $x = 0.33$ doping. The residual resistivity ($\text{at } 4.2 \text{ K}$) for the $x = 0.20$ sample is $\sim 8000 \mu\Omega$-cm with a residual resistivity ratio (RRR) measured from 300 to 4.2 K of $\sim 13$. Clearly, moving from $x = 0.33$ doping to $x = 0.20$ the residual resistivity has increased by about a factor of 16 while the RRR and the metal insulator transition temperature has decreased.

The magnetization as a function of temperature for this $x = 0.20$ sample (figure 5(b)) also indicates a transition to a ferromagnetic phase with an onset temperature, $T_{\text{onset}}$, of around 315 K and a broad foot that extends almost 100 K below $T_{\text{onset}}$ where the shape of the magnetization profile deviates from that of a smooth 2nd order phase transition. As in the case of the previously discussed samples, the small variations in stoichiometry across the sample likely contributes to this high temperature ‘foot’. From fitting to the low temperature magnetization data, a saturation magnetization $M_{\text{Sat}}$ of $\sim 1.8 \mu_B$/Mn was observed. This $M_{\text{Sat}}$ value is similar to that for the $x = 0.40$ sample while significantly smaller than the $M_{\text{Sat}}$ of $\sim 3.7 \mu_B$/Mn measured for the $x = 0.33$ sample. Moreover, the coercive field, $H_c = 0.0283$T, extracted from magnetization versus field measurements made at 5 K for the $x = 0.20$ sample is about a factor of four larger than that found for the $x = 0.33$ sample. All these observations are consistent with the strength of the double exchange interaction becoming weaker as you move in either direction from $x = 0.33$ doping.

What is interesting about the magnetization data for the $x = 0.20$ sample is a small but sudden change in the magnetization around 45 K. The inset to (figure 5(b)) shows a zoomed in view of the low temperature (below 65K) magnetization profile, which has the form of a 2nd order phase transition riding on top of the already ferromagnetic phase. In bulk crystals of La$_{1-x}$Sr$_x$MnO$_3$ around $x = 0.20$ doping a structural transition from rhombohedral to orthorhombic is reported $[5]$ $\sim 100$K where both structural phases are ferromagnetic and metallic. Our observation of a change in the magnetization profile $\sim 45$K for the $x = 0.20$ thin film is suggestive of such a structural transition where both phases are metallic and ferromagnetic, consistent with our observations, although with a change in the strength of the ferromagnetic order parameter.
very small low-temperature saturation magnetization observed, dependent magnetic measurements to the metallic ground state to the electronic ground state. Transport measurements reveal an insulating ground state for by the substrate, as such a transition is not reported in bulk crystals analysis will be needed to understand this. Interestingly, this feature might be related to the epitaxial strain imparted lattice, which alters the strength of the magnetic order parameter, further measurements and careful structural

Figure 9. Transition temperatures, residual conductivity and saturation magnetization as a function of doping. (a) Insulator-to-metal transition temperatures (black solid line) and residual conductivity (blue dashed line) as a function of doping. (b) Temperatures characterizing the onset of magnetic order (black solid line) and saturation magnetization (blue dashed line) as a function of doping, x.

Reducing the doping further—making a small change from $x = 0.20$ to $x = 0.17$—a dramatic change occurs to the electronic ground state. Transport measurements reveal an insulating ground state for $x = 0.17$ in contrast to the metallic ground state (down to 4K) observed for $x = 0.20$ doping. Specifically, electronic transport measurements (figure 6(a)) indicate a transition from insulator-to-metal that occurs $\sim 210$ K as temperature is lowered, immediately followed by a metal-to-insulator transition that occurs $\sim 170$ K, which leads to a re-entrant insulating phase at low temperatures (below $\sim 170$ K). We find the ground state for $x = 0.17$ to be insulating but ferromagnetic: magnetic measurements as a function of temperature measured in a 0.0100 T field (figure 6(b)) indicates a $T_{\text{onset}}$ of $\sim 230$ K, which gradually transitions to a ferromagnetic phase (over a temperature range of $\sim 70$ K). As the sample temperature is reduced, the magnetization approaches a constant saturation value. A fit to the low temperature data shown as a line in figure 6(b) provides a value for $M_{\text{Sat}}$ of $\sim 1.7 \mu_{B}/\text{Mn}$. The coercive field extracted from magnetization versus field measurements made at 5 K for the $x = 0.17$ sample is $H_c = 0.0241$T.

Reducing the doping even further to $x = 0.04$, the absence of any features in the electronic transport measurements (figure 7(a)), indicate an insulating state in the entire temperature range measured. The temperature dependent magnetic measurements (figure 7(b)) reveal, however, an onset of some magnetic order at $\sim 155$ K. But the very small low-temperature saturation magnetization observed, $M_{\text{Sat}} \sim 0.3 \mu_{B}/\text{Mn}$, together with the larger coercive field extracted from magnetization versus field measurements made at 5 K, $H_c = 0.0349$T, indicate that this magnetic ordering is likely due to an antiferromagnetic ordering where the small magnetization signal comes from a canting of antiferromagnetically aligned spins. This is consistent with the A-type (layered) antiferromagnet, spin-canted insulator phase reported in bulk crystals [3, 5]. It should be noted that we also observe a small change in the magnetization profile around 43K. The inset to (figure 7(b)) shows a zoomed in view of the low temperature (below 60K) data. While this could again be due to a structural transition that results in a subtle jahn-teller distortion in the lattice, which alters the strength of the magnetic order parameter, further measurements and careful structural analysis will be needed to understand this. Interestingly, this feature might be related to the epitaxial strain imparted by the substrate, as such a transition is not reported in bulk crystals [3, 5].

Finally we look at the undoped ($x = 0.00$) parent compound, LaMnO$_3$. Even though LaMnO$_3$ is known to be an A-type (layered-type) antiferromagnet in bulk crystals, it has been reported in both theoretical and experimental investigations that a ferromagnetic phase is stabilized when grown as a thin film under epitaxial strain [24, 25]. Specifically, when grown with biaxial strain on STO substrates it has been found to be ferromagnetic when the film thickness is above a critical thickness of 6 unit cells [26]. While the electronic
transport measurements on our \( x = 0.00 \) sample (figure 8(a)), show monotonic insulating behavior in the entire temperature range measured, the magnetic measurements (figure 8(b)) indicate an onset of some magnetic order \( \sim 110 \) K. The low-temperature saturation magnetization, \( M_{\text{sat}} \sim 1.0 \, \mu_B/\text{Mn} \) observed for this undoped parent compound is larger than the \( M_{\text{sat}} \sim 0.3 \, \mu_B/\text{Mn} \) observed for the \( x = 0.04 \) doping. While the saturation magnetization for the undoped compound is still significantly smaller compared to, for example, the \( \sim 3.7 \, \mu_B/\text{Mn} \) value obtained for the \( x = 0.33 \) doping, our measurements provide evidence of a strain driven ferromagnetic order in this undoped parent compound.

It is interesting to note that, compared to that of the other samples, we find an extremely large coercive field for this undoped parent compound. From the magnetization versus field measurements made at 5 K for this \( x = 0.00 \) sample we extract a coercive field, \( H_c = 0.1800 \, \text{T} \). This much larger coercive field points to a different mechanism responsible for the magnetic signal in this parent compound, LaMnO\(_3\), as opposed to the double exchange interaction mediated through itinerant spins in the case of mixed-valent manganites. This magnetic order in epitaxially strained LaMnO\(_3\) thin films provide an interesting test bed to explore the nanoscale control of magnetic order through spin-lattice coupling.

4. Conclusions

Our findings are summarized in figure 9 where we plot the insulator-to-metal transition temperatures (figure 9(a) connected by a black solid line) and the temperatures characterizing the onset of magnetic order (figure 9(b) connected by a black solid line), as a function of doping. The connection between the electronic order and the ferromagnetic order for doping \( x \geq 0.17 \), as mediated by the double exchange interaction is clearly observed both from the close match between the absolute values of the ordering temperatures and the general trend of these ordering temperatures as a function of doping.

We also plot the residual conductivity (figure 9(a) connected by a blue dashed line) and the low-temperature saturation magnetization, \( M_{\text{sat}} \) (figure 9(b) connected by a blue dashed line) as a function of doping. High \( M_{\text{sat}} \) values are accompanied by high residual conductivity values for \( x \geq 0.17 \) indicating that the magnetic order is mediated by the double exchange interaction. The general trend observed in these plots as a function of doping further displays the connection between electronic and magnetic order in these compounds.

Our study provides a starting point to map out a phase diagram for epitaxially strained La\(_{1-x}\)Sr\(_{x}\)MnO\(_3\) thin films grown clamped to the 3.905 Å lattice constant of the SrTiO\(_3\) substrate. It is important to note, however, that the strain state of the strained La\(_{1-x}\)Sr\(_{x}\)MnO\(_3\) thin films on (001) STO substrates studied here is, in itself, a function of doping, \( x \), since the bulk pseudo-cubic lattice constant of La\(_{1-x}\)Sr\(_{x}\)MnO\(_3\) varies from \( \sim 3.87 \) Å [3, 6] for \( x = 0.40 \) to \( \sim 3.94 \) Å [25, 27] for \( x = 0.00 \) (estimated based on the nearly cubic phase \( \sim 750 \) K, the temperature below which Jahn-Teller distortions set-in). The strain state of the films therefore, switches from bi-axial tensile strain to bi-axial compressive strain as \( x \) is reduced from \( x = 0.40 \) to \( x = 0.00 \). Further measurements, especially careful structural analysis and x-ray and neutron diffraction measurements on such films would be needed to probe the implications of strain on the structural, electronic and magnetic properties.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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