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Chapter 3

Manganites

3.1 Introduction to Manganites

Manganites are transition metal (TM) oxides that, like many TM oxides, have a broad range of structural, magnetic, and electrical properties that stem from strong electron-electron and electron-phonon coupling. One example is LaMnO$_3$ (LMO), the parent compound of the manganite studied here. It is a Mott insulator in which the band gap derives from the Coulomb interaction between the d-electrons, unlike simple covalent band insulators. Because of this, the physics of LMO and other manganites is complex, with both orbit and spin playing a crucial role in determining their properties.

In this work the focus is on hole-doped perovskite manganites with the chemical formula, $RE_{1-x}A_x$MnO$_3$, where $RE$ is a trivalent rare earth (La, Nd, Pr) and $A$ is a divalent alkali (Sr, Ca, Ba). They can be regarded as a solid solution of end members $RE$MnO$_3$ and $A$MnO$_3$, with electronic configurations Mn$^{3+}$ and Mn$^{4+}$ respectively. The basic structure of manganites is a pseudo-cubic perovskite structure with Mn at the center surrounded by an oxygen octahedron forming a 3-d network with $RE$ and $A$ at cube corners. This is shown in Fig. 3.1. This basic structure is modified by rotations and distortions of the oxygen octahedra resulting in a rhombohedral or orthorhombic lattice.

Figure 3.1: Manganite pseudo-cubic perovskite structure of type ABO$_3$. Taken from Ref. 58
The particular manganite studied here is Ca-doped LMO or La$_{1-x}$Ca$_x$MnO$_3$. Substituting Ca$^{2+}$ for La$^{3+}$ changes the Mn valence from pure Mn$^{3+}$ to mixed Mn$^{3+}$ and Mn$^{4+}$. This mixed valence plays a crucial role in determining the electronic and magnetic properties. Whereas the parent compound LMO is a canted antiferromagnet (CAF) and an insulator, adding a varying proportion Ca can produce a ferromagnetic insulator (FMI), ferromagnetic metal (FMM), an antiferromagnet (AF), or a charge ordered (CO) phase. This can be seen in the phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ is shown in Fig. 3.2 (left). At elevated temperatures—in the unlabeled portion of the diagram—La$_{1-x}$Ca$_x$MnO$_3$ is a paramagnetic (PM) and an insulator. With doping of $x \approx 1/3$, the transition or Curie temperature ($T_c$) between the FM and PM phase is at a maximum, and is often referred to as optimally doped (LCMO).$^\dagger$ Measured resistivity ($\rho$) as a function of temperature (or RT$^\ddagger$) for close to optimally doped La$_{0.75}$Ca$_{0.25}$MnO$_3$ is illustrated in Fig. 3.2 (right). Shown is an RT curve in zero field and in fields up to 4 Tesla. This illustrates two properties of optimally doped manganites that are of particular interest to this work. The first is colossal magnetoresistance (CMR). This is the large (or colossal) difference between the zero-field resistance and the in-field resistance. The second property of optimally doped La$_{1-x}$Ca$_x$MnO$_3$ is the metal to insulator transition (MIT). Consider the zero-field ($H = 0$) RT curve in Fig. 3.2 (right). The resistance starts low at low temperatures, then increases as the temperature is increased until reaching a maximum at the so called peak temperature ($T_p$). As the temperature increases further, the resistance again drops. The region below $T_p$ is typically described as metallic (meaning $dR/dT > 0$) while the region

$^\dagger$LCMO will refer to all La$_{1-x}$Ca$_x$MnO$_3$ where $x \approx 1/3$. For Ca doping close to this, the film properties are largely the same (see Fig. 3.2).

$^\ddagger$For purposes such as finding $T_p$ an unstructured, 4-point measurement will suffice. In that case an RT measurement will be a resistance versus temperature curve.
above $T_p$ is described as insulating (meaning $dR/dT < 0$).\textsuperscript{56} This transition from metallic to insulating is the MIT. Note that for optimally doped LCMO the PM phase coincides with the insulating phase, while the FM phase coincides with the metallic phase. This is no coincidence. The coupling of FM to metallic and PM to insulating is central to the understanding of CMR and the MIT.

Much of the physics of manganites arises from the electronic structure of Mn. The Mn ion is a transition metal with a five-fold degenerate 3$d$ orbital (see Fig. 3.3). The electrostatic interaction of the Mn 3$d$ orbital with the oxygen 2$p$ orbitals creates a crystal field. This interaction splits the five-fold degenerate 3$d$ orbital into doubly degenerate $e_g$ and triply degenerate $t_{2g}$ levels, with the $t_{2g}$ orbital energy lower than that of the $e_g$ orbital energy.\textsuperscript{58} This is due to their symmetry since they have orbital lobes oriented between the O$_2^-$ ions. The $e_g$ orbitals point towards O$_2^-$ ions and will have higher energy due to Coulombic repulsion. With three $d$-electrons present, an Mn ion will be in the Mn$^{4+}$ valence state, with all three in the $t_{2g}$ orbital and no electrons in the $e_g$ orbital. By Hund’s rules, the spins of the $t_{2g}$ electrons are aligned. Adding a fourth electron creates an Mn$^{3+}$ ion. By Hund’s rules, this fourth electron must go into the $e_g$ orbital with its spin aligned to the $t_{2g}$ core spin. With the $e_g$ orbital occupied, its energy can be lowered if the oxygen octahedral distorts. If, for example, the two apical O ions move further from the Mn ion, the energy of the $d_{3z^2-r^2}$ orbital, which point towards the apical O, will decrease, while the energy of the $d_{x^2-y^2}$ orbital, which point towards the basal-plane O, will increase.\textsuperscript{57,60} The $d_{3z^2-r^2}$ electron will have lower energy with the distortion than without. That the $d_{x^2-y^2}$ orbital energy has increased is irrelevant because there are no electrons occupying it. This distortion is caused by the Jahn-Teller (JT) effect. Conversely, as there are no electrons in the $e_g$ orbital of a Mn$^{4+}$ ion, no distortion takes place. This difference in energy between the occupied and distorted octahedra and the unoccupied but not distorted octahedra results in electron self-trapping in state called a JT polaron. Because charge-carrier...
hopping is the mechanism for conductance, the JT polaron is critical to the electronic properties of manganites.

In general an electron’s kinetic energy is lowered if it can delocalize. In manganites the $t_{2g}$ electrons are localized while the $e_g$ electrons delocalize by hopping between Mn ions. One hopping mechanism available to mixed-valence manganites is through the double exchange (DEX) mechanism. This process involves the exchange of $e_g$ electrons between neighboring Mn ions mediated by the O 2p orbital. One electron from an Mn$^{3+} e_g$ orbital is transferred to an oxygen 2p orbital while simultaneously another oxygen 2p orbital electron is transferred to the $e_g$ orbital of an adjacent Mn$^{4+}$ ion. By Hund’s rule, the $e_g$ electron spin must be aligned with the $t_{2g}$ core spin. Therefore if the $t_{2g}$ core spin of the Mn$^{4+}$ ion is parallel to the $t_{2g}$ core spin of the Mn$^{3+}$ ion, electron transfer will be enhanced. This can be quantified as $t = t_0 \cos(\Theta/2)$, where $\Theta$ is the angle between the core spins.\(^{62,63}\) Delocalization is not only energetically favorable, but also favors alignment of the Mn core moments. Thus delocalization will favor ferromagnetism, with each Mn$^{3+}$ and Mn$^{4+}$ ion contributing a magnetic moment of 4\(\mu_B\) and 3\(\mu_B\), respectively, from their combined $t_{2g}$ core and $e_g$ electron spins. Since it is these delocalized $e_g$ electrons carrying current, FM will be coupled to metallic behavior. Similarly, if the FM alignment of the cores is disrupted by thermal energy—i.e. above $T_c$ in the PM phase, then electron hopping will be reduced, making the material a poorer conductor. By this same reasoning, aligning the core spins with an applied magnetic field enhances DEX and, thereby, decrease resistance. This explains the link between magnetism and transport and offers a simplified explanation of CMR.

Still, DEX alone is not enough to explain the high resistance in the insulator-PM phase.\(^{56,64}\) Misaligned Mn core spins in the PM phase and the consequent scattering of charge carriers does not increase the resistance to the level observed in experiments. An extra ingredient is needed and that ingredient is the JT polaron. As has already been discussed, these form because the presence of an electron in the $e_g$ orbital of an Mn$^{3+}$ ion will favor the JT distortion. With this distortion the electron is now self-trapped. This is a small polaron, so called because the distortion is limited to one Mn and one oxygen octahedron.

The physics of manganites is more complicated than just DEX plus JT polarons. One of the additional complications that has received a great deal of attention is the concept of electronic phase separation (PS). The idea behind PS is that, at some temperatures, the metallic-FM (FMM) phase will coexists with the insulating-PM phase (PMI).\(^{65}\) The proportion of each phase is expected to vary depending upon the temperature. At very low temperatures the FMM phase will predominate. All conduction will follow a pathway through the metallic phase, shunting any remaining insulating phase. As the temperature is increased towards the transition temperature, the insulating regions will begin to grow. At temperatures close to the MIT temperature, the proportion of insulating and metallic phases will reach a critical level, with small changes in temperature resulting in large changes in resistance. A small increase in temperature will change the FMM phase from connected across the sample to metallic islands in an insulating matrix. Once the metallic regions are reduced to islands, current will have to flow through the some of the insulating phase to get from
metallic island to metallic island. At this temperature, the resistance will increase dramatically, producing the jump in resistance observed RT measurements. The PS model can also explain CMR. In this case the effect of an applied magnetic field is to bolster ferromagnetism, enlarging the FMM phase at the expense of the PMI phase. At temperatures close to the MIT, these enlarged FMM phase islands can coalesce into percolation pathways, producing a dramatic drop in resistance.

Although this model provides a nice explanation of the MIT and CMR, there are still unanswered questions about the details of phase separation. In particular the connection between disorder and the temperature and spatial ranges where PS can be observed, and the connection to transport experiments, still deserve attention.

Local-probe techniques, such as scanning tunneling microscopy (STM) and magnetic force microscopy, would seem to be ideal tools to explore these questions, and a number of groups have applied them to the study of manganites. Overall, the literature on PS in manganites is conflicting, with some researchers finding evidence of PS and others not. There are good reasons to carefully scrutinize results from surface-sensitive techniques such as STM. Extensive investigations, both experimentally and theoretically, have indicated that manganite surface properties differ from those of the film bulk.

Nevertheless, from STM and STS measurements of thin-film manganites, evidence of half-metallicity, polarons, and pseudo-gaps have all been claimed, while spatial electronic PS has been mapped as a function of both applied magnetic field and temperature. These surface-sensitive measurements are purported to represent bulk properties, but, in light of our results presented here, we must emphasize caution when interpreting them as such. As a further caution, we note that the STM/STS measurements reported in the literature cited above were made on a variety of manganite systems. It should be realized that spatial inhomogeneities could be significantly different for wider bandwidth systems such as La$_{1-x}$Sr$_x$MnO$_3$ or narrower bandwidth systems such as La$_{1-x}$Ca$_x$MnO$_3$; or for differing strain states such as fully strained versus (partially) relaxed.

### 3.2 Experiment

We confined our STM/STS study to thin-film La$_{0.67}$Ca$_{0.33}$MnO$_3$. At this doping level the material should be a paramagnetic insulator above the MIT and ferromagnetic metal below. We varied thickness, strain, and surface morphology. Our strained films were grown on SrTiO$_3$ (STO) substrates and minimally strained (unstrained) films on NdGaO$_3$ (NGO) substrates. The film thickness was varied between 10 and 180 nm by changing deposition time, and we found that film surface morphology varied with film thickness—thicker films were rough while thinner films were atomically smooth. Strained films 40 nm or thinner were coherently strained, while unstrained films remained coherent up to 180 nm, the thickest film grown. We then compare our results to the above.
surface-sensitive STS measurements to bulk-sensitive measurements of these same films. We found that STS measurements of atomically smooth films did not vary significantly with lateral position and the surface was therefore electronically homogeneous, while STS measurements on rough films did vary spatially and the surface was thus inhomogeneous. Further, STS measurements on spatially homogeneous films were only weakly modified by changes in temperature or applied magnetic field, and are thus electronically and, because of the expected coupling of the MIT to \( FM-PM \) transition, magnetically inactive. Nevertheless, bulk-sensitive measurements indicate that all of our films exhibit both CMR and a MIT.

### 3.2.1 Growth and Characterization

Thin films of LCMO with thicknesses between 10 nm and 180 nm were grown on single crystal substrates of \( \text{SrTiO}_3(001) \) and \( \text{NdGaO}_3(001) \). All films were grown using dc sputtering from stoichiometric targets in 3 mbar of pure oxygen. The film thickness was taken from sputtering time and verified with X-ray reflectivity measurements of selected films (see below for details). Various substrate temperatures were used during film growth, all between 780 °C and 840 °C. Some films were annealed \textit{in-situ}, immediately after sputtering. Others were annealed \textit{ex-situ} in flowing pure oxygen at atmospheric pressure. Surface morphology was verified with tapping-mode atomic force microscopy.

Resistance (R) versus temperature (T) measurements were made using four in-line probes attached to the film with either silver paste or indium, or using structured bridges. For unstructured measurements, as the probes were of variable size and with variable distance, only resistance and not resistivity was obtained. Nevertheless, normalized RT curves are sufficient to observe the MIT and CMR and to characterize film quality. X-ray diffraction (XRD) measurements were made with a Siemens D5005 using a Cu K\( \alpha_1 \) source. Film thicknesses were determined using low-angle XRD, while film quality was verified with Laue oscillation measurements. The film strain was determined by measuring \{00l\}, \{103\}, and \{203\} planes using a Panalytical Xpert Pro MRD with a Cu K\( \alpha_1 \) source. X-ray photoemission spectroscopy (XPS) measurements were made using a Mg anode (1253.6 eV) and hemispherical analyzer in a UHV measurement chamber with base pressure on the order of \( 10^{-10} \) mbar. Samples were either baked overnight in a load-lock at approximately 100 °C to desorb surface contaminants, or brought into the measurement chamber rapidly to retain any contamination present on the sample surface. Some films were plasma etched using both \( \text{O}_2 \) and \( \text{Ar} \) at a calibrated etch rate of 1 nm/minute. This combination has been shown to etch \( \text{SrTiO}_3 \) without depleting its oxygen and thus rendering it metallic.\(^{84}\)

### 3.2.2 STM

STM measurements were made under various conditions, ultra high vacuum (UHV), flowing helium gas, and ambient. All of our STM heads were built in-house and use a coarse approach based upon the Pan design, as described in Ch. 2.\(^5\) Both
mechanically cut PtIr (90%:10%) and electrochemically etched Pt wires were used as STM tips. The UHV STM chamber has a base pressure of $4 \times 10^{-10}$ mbar, with the capability to vary the sample temperature between 300 mK and 180 K and the possibility to apply magnetic fields up to 10 T. Samples were brought into the UHV chamber after being pumped overnight in a load-lock.

Other STM measurements were conducted in helium boil-off gas within a variable temperature insert (VTI) mounted in the bore of a 12 T magnet. Using resistance heating, the sample temperature can be varied between 4.2 and 340 K. Once inserted into the cryostat, samples were held between 300 K and 340 K while being flushed with dry helium gas to effect desorption of contaminants. To minimize the sample cryopumping while at low temperatures, samples were kept warmer than the surrounding VTI. Ambient STM measurements were made using the same STM as used for helium gas measurements, but without inserting the STM into the VTI. Which STM was used is noted in the Figure captions.

Current-voltage curves ($I$-$V$) were measured using a fixed tunneling gap method. This begins with the STM in tunneling at particular bias ($V_{\text{set}}$) and current ($I_{\text{set}}$) set-points and with the feedback engaged. The STM feedback is then disengaged, freezing the tip-sample distance, while the bias voltage is swept through the desired voltage range ($V_{\text{sweep}}$). Simultaneously, both the applied bias voltage and the measured tunneling current are recorded. Up to 500 curves were taken and averaged for each $I$-$V$ curve. Measured $I$-$V$ curves were numerically differentiated after averaging.

![Figure 3.4](image-url) Figure 3.4: Resistance versus temperature curves normalized to the zero-field peak resistance. The solid curve is of a 10 nm $La_{0.67}Ca_{0.33}MnO_3$ film grown on SrTiO$_3$, measured in the indicated magnetic fields ($T_p \approx 145$ K). The dashed curve is of a 26 nm $La_{0.67}Ca_{0.33}MnO_3$ film grown on NdGaO$_3$ ($T_p \approx 260$ K).
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Resulting \( dI/dV \) spectra were used as a proxy for sample density of states (DOS). Because an I-V curve is a convolution of the sample DOS with the tunneling barrier and tip DOS, and because of the difficulty of separating out each component,\(^{53,85}\) we prefer to compare only \( dI/dV \) spectra measured at identical \( V_{set} \) and \( I_{set} \). As has already been discussed, we cannot define metallic and insulating in absolute terms, but only in terms of comparing one spectrum to another spectrum. A more metallic spectrum would thus have a larger zero-bias conductivity and flatter overall shape.

Conductance maps were measured using a digital lock-in amplifier. While scanning topography, the STM bias voltage (\( V_{bias} \)) was modulated with an ac voltage (\( V_{ac} \)) from an oscillator built into the lock-in amplifier. The ac modulation was limited in amplitude to a few percent of the bias voltage, and at a frequency higher than the feedback bandwidth (on the order of 1 kHz). Conductance was computed by the lock-in using output from the STM current-to-voltage amplifier. The conductance measured in this manner is thus the conductance at \( V_{set} \). As the absolute conductance is strongly dependent upon the tunneling gap and both the tip and sample DOS, conductance maps will be normalized to its mean value. Because the tunneling gap should remain approximately constant for a given \( V_{set} \) and \( I_{set} \), any variation of conductance is ascribable to the sample DOS. These maps are normalized by the average conductance.

3.3 Results

3.3.1 Morphology

With increasing film thickness, we observe that, for films grown on both NGO and STO, the surface changes from flat with unit-cell step heights, \( \approx 0.4 \) nm, to a rougher morphology, 5 to 20 nm peak-to-peak, with no indication of terraces or islands. We also observe that flat films can be further divided into those with long narrow terraces and those exhibiting 2-D island growth. Typical examples of terraced and 2-D island growth morphology are shown in Fig. 3.5. Both of these films are 10 nm thick, were grown on STO substrates, and measured with an STM in ambient conditions. Although for films grown on STO with thicknesses between 10 and 50 nm both morphologies were found, the predominant morphology was terraced. Since growth conditions were nominally the same, we attribute the occasional appearance of island growth to the varying quality of the commercial substrates used. However, other researchers have noted a change from terrace growth to 2-D island growth for LCMO grown on low miscut-angle STO as films thickness is increased above 30 nm.\(^{86}\) For our thicker films on STO, those about 100 nm and thicker, the surface morphology is usually rough. Terraced and 2-D island growth was also seen for films grown on NGO and are similar in appearance to the STO films shown in Fig. 3.5. However, for films grown on NGO, a correlation between film thickness and surface morphology is apparent. The thinnest films, around 10 nm thick, were almost exclusively terraced. Medium thickness films, around 25 nm thick, generally exhibited 2-D island growth.
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Figure 3.5: Ambient STM images of typical terraced, (a), and island, (b), topography for \( \text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3 \) grown on \( \text{SrTiO}_3 \) substrates. Films are 10 nm thick. Both images exhibit unit-cell step heights.

Thicker films, those thicker than 50 nm, were usually rough.

X-ray measurements of in-plane and out-of-plane lattice parameters for films grown on STO show them to be coherently strained for thicknesses up to 40 nm. Because of almost matching lattice parameters between film and substrate, films grown on NGO were coherent at all film thicknesses grown (up to 180 nm).

Transport measurements were made on some of our films. Shown in Fig. 3.4 are example RT measurements for flat LCMO films grown on STO and NGO. From such curves we can extract the peak temperature \( T_p \). These curves were normalized to the zero-field peak resistance. The peak temperatures are typical for strained films grown on STO \( (T_p \approx 145 \text{ K}) \) and unstrained films grown on NGO \( (T_p \approx 260 \text{ K}, \) close to the bulk value), though \( T_p \) does vary a little with film thickness. Also shown for the STO film is an RT measurement in magnetic field that confirms this film to be strongly magnetoresistive. Similar measurements were made of other films, both flat and rough. We can conclude that the film bulk of both our flat and rough films have an MIT and are magnetoresistive.

XPS measurements were made of a subset of films to confirm the presence of lanthanum, calcium, manganese, and oxygen and to verify the absence of other, contaminating elements at the film surface. Except for carbon, no evidence of contamination was observed. Since carbon contamination is ubiquitous, and as sample cleaning was limited to moderate in-situ heating, the presence of carbon is not unexpected, and does not necessarily indicate a poor quality film.\(^{87}\)

3.3.2 STM

STM and STS measurements were taken of LCMO films with various thicknesses grown on STO and NGO substrates. Both flat films, those with terraced or 2-D island growth, and rough films, those with rounded morphology and no discernible
unit-cell steps, were measured.

**Rough Morphology**

Thicker LCMO films grown on either STO or NGO were generally rough and those that were rough showed compelling evidence of both electronic PS and magnetically active surface layers. Both conductance maps and $dI/dV$ spectra of rough films demonstrate that they were phase separated and magnetically active.

First we consider conductivity maps and $dI/dV$ spectra of a rough film grown on NGO. An example of topography and conductance map of such a film is shown in Fig. 3.6(a) and (b), respectively. The lines on these images correspond to cross sections plotted in Fig. 3.6(c) and (d). The section through the conductance map shown in Fig. 3.6(d) has been normalized with the average conductance of the line. This film was 50 nm thick with, as was typically seen on thicker films, rough topography ($\approx 8$ nm peak-to-peak). As is evident from the conductance map and corresponding section line, the sample appears inhomogeneous, with conductance varying $\pm 5\%$, with areas of high and low conductance extending from 10 to 20 nm. Note that there is significant correlation between the conductance map and topography. This is not because of feedback-error, since the forward and reverse scans of the conductivity map are very similar, but rather reflects properties of the film surface. Although this particular measurement was made at 280 K, just above $T_p$ (260 K), where PS would not yet be expected, other conductance maps of this film recorded above and below $T_p$ were similarly inhomogeneous. As further confirmation of the apparent inhomogeneity seen in conductance maps, $dI/dV$ spectra were also taken of this film. Spectra taken at various locations indicate that the surface electronic structure of this film varies significantly. Shown in Fig. 3.6(e) and (f) are examples of $I$-$V$ curves and corresponding $dI/dV$ spectra taken of this film. Both curves were measured at 299 K, well above $T_p$, but at different locations. As can be seen in (f), the zero bias conductivity of these two curves differ by almost an order of magnitude, from $6.5 \times 10^{-11}$ to $6.1 \times 10^{-10}$ siemens. One of the curves is also significantly flatter. Given the caveat mentioned above, the flatter curve with the higher zero-bias conductance can be reasonably described as the more metallic of the two. These curves demonstrate that even well above $T_p$, rough films are inhomogeneous. Other $dI/dV$ spectra measured at and well below $T_p$ also indicate electronic inhomogeneities as do measurements of other rough films.

Next we look at rough films grown on STO. To do this we measure conductance maps at the same location but in different magnetic fields. If the film surface is magnetically active then, because of the coupled $FM$-$PM$ and MIT transitions and because LCMO should exhibit a CMR effect, we expect to see changes in the electronic structure as the applied field is changed. Such a measurement of a 100 nm thick rough film grown on Nb-doped STO is shown in Fig. 3.7, with peak temperature of about 250 K. The film topography in shown in (a). The surface is rough, with peak-to-peak height variations of $\approx 12$ nm. Also shown in Fig. 3.7 is a sequence of conductance maps covering the same area as shown in (a), but for different applied magnetic fields,
Figure 3.6: STM measurements of a rough 50 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on NdGaO$_3$. Its peak temperature $T_p$ is 260 K. (a) Topography, (b) conductance map, (c) section through topography, and (d) normalized section through conductance map. Measured simultaneously at 280 K in zero magnetic field. $V_{\text{set}}=-0.5$ V, $I_{\text{set}}=0.5$ nA, and $V_{\text{ac}}=10$ mV. (e) $I$-$V$ measurement and (f) corresponding $dI/dV$ spectra. Measured at 299 K at different locations on the film. $V_{\text{set}}=-0.5$ V, $I_{\text{set}}=0.5$ nA, $V_{\text{sweep}}=\pm 1$ V. All measured in Helium gas.
Figure 3.7: STM measurements of a rough 100 nm thick La$_{0.67}$Ca$_{0.33}$MnO$_3$ film grown on Nb-doped SrTiO$_3$ substrate. Its peak temperature $T_p$ was about 250 K. All images are 500 nm$^2$. Topography is shown in (a). Conductance maps with applied magnetic fields of 0, 2, 4, 6, and 7 tesla are shown in (b), (c), (d), (e), and (f) respectively. Darker areas are more insulating and lighter areas are more metallic. (g) Section through topography and (h) normalized section through zero-field conductance map. Measurements made in helium gas at 50 K (far below $T_p$), $V_{set}=-2.0$ V, $I_{set}=0.2$ nA, and $V_{ac}=24$ mV.
0 through 7 tesla. What is apparent is that as the applied field is increased, the area of the metallic phase (light) increases while the area of insulating phase (dark) decreases. But not only does the total area of the metallic phase increase, the metallic regions coalesce, connecting together in a manner consistent with percolation. Although the predominant trend is an increase in the metallic phase, there are some places where the insulating phase enlarges at higher fields. There is some correlation between surface morphology and conductivity, though not as significantly as seen in other films (see Fig. 3.6). Because the surface electronic structure responds to an applied magnetic field, we would describe this film as magnetically active. These conductivity maps were measured at 50 K, well below the MIT temperature, yet electronic inhomogeneities were still present, even with a 7 Tesla applied magnetic field. Other measurements of rough films grown on NGO show them to be magnetically active—i.e., conductance maps are more metallic with an applied magnetic field than without. This, combined with the results of our other STM measurements, suggests that electronic inhomogeneities are a robust feature of the surface of rough films.

Smooth Morphology

Thinner films grown on either NGO or STO were typically atomically smooth. When atomically smooth, these films were also electronically homogeneous. That is to say, $dI/dV$ spectra measured at different locations on the film surface were substantially the same, while conductance maps were substantially featureless. In addition, we would describe the surface of our atomically smooth films as magnetically inactive. This is because an applied magnetic field of up to 8 T did not result in a significant change in $dI/dV$ spectra or conductance maps, regardless of the sample temperature. We measured many atomically smooth films, but present data from only three representative films, two grown on STO and one grown on NGO.

First we examine the conductance map of a 10 nm thick film grown on STO and compare it to that of a rough film. Topography and conductance maps for this film are shown in Fig. 3.8(a) and (b), respectively. This measurement was made in zero magnetic field at 150 K, close to the film’s $T_p$ (about 145 K, see Fig. 3.4). We chose this temperature because, for a first-order phase transition, we would expect to see the most pronounced electronic inhomogeneities close to or at the phase transition temperature. However, as can be seen in (b), we saw no evidence of PS at this temperature. Other conductance maps taken at other temperatures are similarly featureless. What detail there is in this conductance map is at terrace edges and defects. We attribute this to feedback error, the increased or decreased conductance resulting from the tip coming closer to or going further away from the surface. To allow comparison of the conductance maps of rough and smooth films, plotted in Fig. 3.8(c) is a normalized section through the conductance map of this film (solid line) and the conductance map of the rough film shown in Fig. 3.6 (broken line). What is apparent is that the section line through the rough film deviates from the average by a greater amount and remains away from the average for longer. This suggests that the rough film was more varied electronically, and that these variations were
more clustered. Changing the STM bias voltage, current set point, or ac-modulation voltage did not alter this finding. The conductance map in Fig. 3.8 was measured at $V_{set}=-3.0$ V, $I_{set}=3.0$ pA, $V_{ac}=8.0$ mV. (c) Normalized section through conductance maps of this film (green) and the rough film from Fig. 3.6 (red).

Secondly we will examine $dI/dV$ spectra taken of smooth films, one grown on NGO and the other on STO. As will be shown, the spectra of these two films vary little with temperature, spatial position, or applied magnetic field.

Shown in Fig. 3.9 are $dI/dV$ spectra measured on an atomically smooth 26 nm...
Figure 3.9: STS measurements of a smooth 26 nm thick La$_{0.67}$Ca$_{0.33}$MnO$_3$ film grown on NdGaO$_3$. Its peak temperature $T_p$ was 260 K. (a) Numerically differentiated $I$-$V$ curves in zero magnetic field at indicated temperature. (b) Spectra from (a) normalized by dividing through by $I/V$; see text for details. (c) Numerically differentiated $I$-$V$ curves at 265 K at indicated magnetic field. (d) Conductance calculated from numerically differentiated $I$-$V$ curves in zero magnetic field. $V_{set}=-0.7$ V, $V_{sweep}=\pm 1.0$ V, $I_{set}=1.0$ nA. Measured in helium gas.
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thick film grown on NGO (\(T_p = 260\) K, see Fig. 3.4). Spectra taken above, at, and below the \(T_p\) of this film (260K) are shown in (a). These three curves are very similar. (d) shows the zero-bias conductance from both the spectra shown in (a) and other spectra measured on this film. There is little variation in the zero-bias conductance. In contrast, the RT measurement of this film, shown in Fig. 3.4, indicate a dramatic change in resistance over the same temperature range. Also plotted on Fig. 3.9(d) is the set-point and negative set-point conductance for these curves (the negative set-point conductance is the conductance at a bias with the opposite polarity but same magnitude at \(V_{set}\)). The set-point conductance does not change significantly, though there is no reason to expect it not to. Compare this to changes in the set-point conductance from the rough film shown in Fig. 3.6. On this rough film, the set-point conductance varies from \(1.5 \times 10^{-9}\) to \(3.5 \times 10^{-9}\) siemens. Further, qualitatively the metallic and insulating \(dI/dV\) spectra measured on the rough films are quite different, while the spectra measured on the flat film are largely the same. Although the set-point conductance of the flat film does not vary much, both the zero-bias and negative set-point conductance do. We believe that variation in the negative set-point conductance is attributable to vertical drift occurring while the feedback is disengaged, rather than variation in the film properties. This was generally the case, to a greater or lesser extent, for all \(dI/dV\) spectra measured. Reversing the \(V_{set}\) polarity does not change this finding. As can be seen in (a) and (c), the \(dI/dV\) spectra are consistently noisier on the negative set-point side. This we believe is because of drift while the feedback is disengaged. We suspect that variations in the zero-bias conductance seen in (d) were also caused by drift.

Shown in Fig. 3.9(b) are the \(dI/dV\) spectra from (a) but normalized by dividing by \(I/V\). Normalizing in this way attempts to extract the DOS from the \(dI/dV\) spectra by canceling the effect of the tunneling gap as discussed in Chapter 2.\(^{54}\) While these normalized curves appear noisy, very little smoothing was performed on the \(I-V\) curves or \(dI/dV\) spectra before the normalization procedure and no smoothing at all was performed after normalization. We minimized smoothing to reduce any distortion that smoothing can introduce. Using a similar normalization procedure, earlier studies claimed to observe both polaron peaks\(^{69,82}\) and half-metallicity\(^{82}\) on manganite films. We measured \(dI/dV\) spectra from many flat films grown on either STO and NGO and normalized these spectra with this method. While occasionally our data did suggest polaron peaks, these peaks did not appear on all films, even if grown under identical process conditions, nor at all measured temperatures. When polaron peaks were evident, the peak-to-peak gap varied little with temperature, and no trend, such as seen by Seiro et al\(^{69}\) was apparent.

Figure 3.9(c) displays \(dI/dV\) spectra measured on this same film but in a 0 and a 5 Tesla magnetic field. These data were taken at 265 K, close to the MIT of this film (260 K). These spectra are very similar to each other and to other spectra taken on other parts of the film, and also to spectra taken at other temperatures. Any differences are attributable to experimental error and show no correlation with either temperature or magnetic field. As we expect a large negative magnetoresistance in the vicinity of the MIT, this result suggests that the film surface is magnetically inactive.
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Figure 3.10: STS measurements of a smooth 10 nm thick La$_{0.67}$Ca$_{0.33}$MnO$_3$ film grown on SrTiO$_3$. Its peak temperature $T_p$ was 145 K. Numerically differentiated $I$-$V$ curves (a) in zero magnetic field at indicated temperature and (b) at 121 K at indicated magnetic field. (c) Conductivity calculated from numerically differentiated $I$-$V$ curves in zero magnetic field. $V_{set}$=1.0 V, $I_{set}$=0.5 nA, $V_{sweep}$±1.0 V. Measured in UHV.
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Similar results were seen on flat films grown on STO. Fig. 3.10 shows $dI/dV$ spectra measured on a 10 nm thick La$_{0.67}$Ca$_{0.33}$MnO$_3$ film grown on SrTiO$_3$ which had a $T_p$ of 145 K (see Fig. 3.4). Little variation is seen as a function of either temperature, (a), or magnetic field, (b). While the zero-bias conductivity, (c), is varied, it appears to be just noise because no trend is apparent over a temperature range of 170 to 4K. STS measurements of other films grown on STO were similar, while transport measurements of these films show both a MIT and CMR. Whatever underlies the MIT and CMR is not apparent in STS measurements of our flat films.

Etching and Annealing

We attempted to remove the electronically inactive layer observed on flat films using a plasma etch. Similarly to Hudson et al, we found that once etched, the film surface became electronically active, but that the results were inconsistent from sample to sample. Etching 1 or 2 nm did modify the $dI/dV$ spectra, but did not result in the appearance of metallic spectra (meaning a significant increase in zero-bias conductivity). After etching about 3 nm, we were able to measured some metallic $dI/dV$ spectra. On these films we typically measured a number of metallic $dI/dV$ spectra at temperatures somewhat below $T_p$. The typical temperature window for this metallic behavior was between 5 and 15 K wide. However, upon cooling to lower temperatures, the metallic phase was no longer evident, and instead of remaining metallic, the $dI/dV$ spectra became insulating and similar to those seen above the transition. Atomic force microscopy images of etched films show that etching initially followed the existing topography, leaving terraces with an appearance similar to as-grown. Further etching (3 nm or more) rounded off terrace edges, roughening the film, and giving it the appearance of an as-grown rough film. Etching did not produce spectra consistent with the MIT seen in transport measurements of these films, and it is unlikely that our STS data are representative of film-bulk behavior. This indicates that etching does something more than simply remove an inactive surface layer, and thereby exposing—which we know to be—the active film-bulk material.

One possible explanation for the inactive surface layer is oxygen depletion. We attempted to re-oxidize films by annealing them in an oxygen-rich atmosphere. One sample was annealed $in-situ$ in 1000 mbar of oxygen at 650°C for 30 minutes. This sample proved to be electronically inactive. We also tried to eliminate possible causes of oxygen depletion. Although our films were typically grown in 3 mbar of oxygen, our usual process recipe called for evacuating the process chamber immediately after sputtering was complete. Thus while cooling, the film would be exposed a vacuum on the order of $1 \times 10^{-6}$ mbar. Beyreuther et al found below-stoichiometry oxygen in manganite films exposed to UHV at elevated temperatures (470-670°C), and so we attempted to minimize film de-oxidization by maintaining 3 mbar of oxygen during cooling. The resulting film was still electronically inactive. Beyreuther et al were able to re-oxidize their films by annealing them in oxygen. We attempted to do the same by annealing a film at 470°C in flowing oxygen for 3 hours, but the annealed film was roughened by the process (see Fig. 3.11). Now that the surface was rough, the film was
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At this point, an obvious question is: what can we say from the STM data with respect to the issue raised in the Introduction with respect to disorder, and the temperature and spatial ranges where PS can be observed. Moreover, since we also observed electronically inactive films which otherwise showed MI transitions, the question is how to reconcile these data. Finally, it is useful to place the results in the context of other published results and different types of measurements.

3.4.1 Phase Separation

Our results show a strong correlation between film topography and electronic homogeneity. Our rough films, with a crystalline-grain morphology are phase separated, while our smooth films, with a terraced morphology are homogeneous, but dead. The results on rough films reproduce the earlier Leiden work. Another publication reports PS and field-induced percolation, but on a flat film. Other researchers report PS on a rough film, but find that an applied field induces an overall increase in conductivity, not percolation. Finally, a number of researchers report electronically homogeneous films that, unlike our flat films, are electronically active. These homo-
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geneous films will be discussed in Section 3.4.2. Our measurements of flat films likely stem from an inert surface layer that completely masks the properties of the film bulk. It is of interest to discuss whether this has an intrinsic nature, which will be done in Section 3.4.3. It will be noted that there is little agreement between published reports, and quite a few reports that are in direct conflict.

Evidence from Scanning Probe Microscopy

In agreement with our data, other researchers have measured PS on rough films with a surface characterized by crystalline grains. In an early experiment performed at Leiden, Fäth et al detected PS on a rough (maximum 20 nm peak-to-peak roughness) LCMO film grown on STO. This is shown in the left side of Fig. 3.12. It is apparent that as the field is increased, the areas of the film with insulating character (light areas) decrease, while the areas with a metallic character (dark areas) increase. The result is an enlargement of metallic areas until they merge, leading to a percolation of connected metallic areas across the film. Once there are pathways of contiguous metallic regions, the film resistance will be greatly reduced. This is as would be expected if PS were the underpinning of CMR. We have demonstrated exactly the same effect on rough films grown on STO (see Fig. 3.7) and NGO (not shown).

Similarly, evidence that PS and metallic percolation underlie the MIT was pre-
They measured zero-bias conductance (ZBC) maps\(^\dagger\) of both an LCMO film and a La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) film. Both films were electronically inhomogeneous and both films had a rough, grain-like surface morphology. While the LCMO film was only measured at room temperature, the Sr-doped film was measured at several temperatures (see right side of Fig. 3.13).\(^67\) As the film temperature was increased, the area of metallic phase (light) decreased while the area of insulating phase (dark) increased. In the highest temperature map (278 K), the metallic regions are small and disconnected. But in the lowest temperature map (87 K), the metallic regions have expanded until contiguous, forming metallic percolation paths throughout the image. This picture is consistent with PS plus percolation model of the MIT.

Beyond these two publications the PS picture becomes less clear. Chen \textit{et al.} also observed electronic inhomogeneities on a rough LCMO film grown on STO.\(^68\) Their film was 300 nm thick with peak-to-peak height variation of 7 nm over 50 nm lateral distance, with no evidence of terraces or unit-cell steps. Just below T\(_c\) they detected PS, but with metallic regions limited to small patches. In field these patches enlarged, but not sufficiently to coalesce and form percolation pathways. At 100 K, well below T\(_c\), the area of metallic phase had greatly expanded. Applying a field at this temperature had little effect on the size or distribution of the metallic phase, but this behavior is expected at this temperature, well into the metallic phase, where the film should already be predominantly metallic.

Magnetic force microscopy (MFM) offers the possibility to directly measure the local magnetic properties of LCMO films. One of the advantages of MFM over STS is that it is not as surface sensitive and can penetrate some distance into the sample. While STS is limited to exploring the uppermost few nanometers of a surface, MFM can effectively measure tens to hundreds of nanometers below the sample surface.\(^91\) Biswas \textit{et al.} measured MFM of LCMO films grown on both LAO and NGO.\(^70\) The LAO film proved to have a rougher and grainier surface than the NGO film. At 80 K, well below T\(_c\), the MFM images of the LAO film had more contrast than the images of the NGO film. The authors attributed this contrast to two-phase behavior stemming from strain variation on the grainy LAO surface. The NGO film was unstrained and, presumably, homogeneously so, and thus single phased. It should be noted that STS and MFM measure very different properties. MFM measures the surface magnetization and STS measures the surface electronic properties. It is only our expectation that the electronic and magnetic properties of LCMO are correlated that makes a comparison of STS and MFM measurements valuable at all.

Unfortunately the picture is no clearer from the perspective of MFM measurements. Chung \textit{et al.} also performed MFM of LCMO grown on LAO, but found somewhat a somewhat different result.\(^92\) Again the film surface was rough, with 100 to 200 nm grains. At room temperature, above the films T\(_c\) (235 K), there is little contrast in the MFM image, indicating a lack of magnetic features. However at 150 K, well below T\(_c\), the image has high contrast, with contrast domains of 500 to 1000

\(^\dagger\)The zero-bias conductance is taken from the slope of the IV curve at V\(_{bias}\) = 0. A ZBC map requires that a grid of IV curves be measured, with at least one IV curve per pixel.
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Figure 3.14: Topography and STS from Köster et al on a layer-by-layer grown LCMO film.\textsuperscript{90} Topography (left). STS of the same film measured at 267 K ($T_p = 270$ K). Measured in zero field (center) and 4 T (right). All images 250 x 250 nm$^2$.

nm extent. The authors attribute the MFM image contrast to domains of in-plane magnetization, not electronic PS, implying, therefore, that the film was uniformly ferromagnetic. In this work there seemed to be much less correlation between film morphology and ferromagnetic domains; the film grain size is quite different from the magnetic domain size. From this measurement it appears that a rough, grainy LCMO film can be homogeneously ferromagnetic.

Only one other group has presented STM/STS data showing conductance maps of both flat and rough films.\textsuperscript{90,93} In one publication Moshnyaga et al measured LCMO films on MgO at 115 K, significantly below the film’s MIT temperature.\textsuperscript{93} They found their flat film to be electronically homogeneous, while their rough film was inhomogeneous. They also studied the structure of these films with high-resolution electron microscopy and electron diffraction. From this they determined that the smooth film was A-site ordered while the rough film was A-site disordered.\textsuperscript{†} From this evidence they concluded that the electronic PS was due A-site disorder. Though the films differed in terms of A-site ordering and PS, the CMR ratio of the ordered and disordered films were similar, though not identical; both the MIT and PM-FM FM transition were sharper in the ordered film. From this they conclude that there are two types of CMR with different underlying mechanisms, despite manifesting themselves with similar magnetic and electronic properties. The first model incorporated PS, with some amount of disorder to support PS (A-site disorder for their film). The second model required no PS and instead proposed that the homogeneous film be close to a CE-AFM/FM phase boundary.

In later work from the same group, they compared 3-D growth mode (rough) films to layer-by-layer growth mode (smooth) films. STS measurements were made of these films as a function of applied magnetic field, at temperatures close to their respective $T_p$.\textsuperscript{90} They detect PS on both films, though the PS was more pronounced on the

\textsuperscript{†}A-site comes from the general formula for ABO$_3$ perovskites. For manganites, B is Mn while A is, typically, a rare earth (La, Nd, Pr) or an alkaline earth metal (Ca, Sr, Ba).
Figure 3.15: Topography and STS from Hughes et al of terraced LCMO film. Topography (left). STS of the similar film measured at 6 K ($T_p 270 \pm 10$ K). Measured in (a) zero field, (b) -0.3 T, and (c) 3 T.

rough film. Results of measurements of the smooth film displayed in Fig. 3.14. On the left side is a topographic image of the layer-by-layer growth mode film. In the center is a ZBC map taken of the same film in zero field while in the right side is a ZBC map taken in 4 T. In an applied magnetic field both films became more conductive, although in neither film do the metallic regions appear to percolate. Instead both films seem to have a static PS, with only overall increases in conductivity, and no metallic phase percolation. They report that varying the measurement temperature produced a similar shift in overall conduction, with no evidence of percolation. These results certainly suggest that percolation is not a necessary part of CMR.

In one very recent publication, Hughes et al measured spin-polarized (sp) and non-sp STS of flat, terraced LCMO films. From constant-bias conductance maps they found their films to be phase separated at all temperatures, even down to 6 K. This was true even though their films were flat, with wide terraces separated by unit-cell high steps (see Fig. 3.15). Conductance maps measured in the paramagnetic state (300 K) were more homogeneous than those measured in the ferromagnetic state (77 K). Applying a magnetic field resulted in more homogeneous conductance maps, and not the static PS seen by Köster et al (compare Fig. 3.15 to Fig. 3.14). They suggest that there use of high-bias STS allows them to probe through a surface dead

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1Perhaps percolation would have been detected if they processed their data in the same way as was done by Becker et al. In that publication, the conductance maps were presented in a binary fashion using a zero-bias conductance threshold rather than a gray scale. One can imagine that apparent percolation could be seen as more areas cross the threshold, and are then assigned to the metallic bin. This is analogous to a flooded landscape. At first only the mountain peaks are visible. As water recedes, these mountain peaks begin to merge, forming isolated ridges. Finally, the ridges merge and all is left are isolated lakes of water. In all of this the shape of the mountains has not changed.
Evidence from Other Techniques

As STS is inherently surface-sensitive it would be instructive to have evidence from less surface sensitive measurements to help understand the role of PS in CMR.

Bibes et al measured a series of LCMO films with varying thickness with NMR.\(^{94,95}\) Measuring at 4.2 K, they found the signature of both a Mn\(^{3+}/4^+\) mixed state (corresponding to the ferromagnetic metal (FMM) phase) and of a Mn\(^{4+}\) dominated state which they assigned as a ferromagnetic insulator (FMI) phase. Moreover, they found a non-FM insulating phase of approximately 5 nm thickness located, most likely, adjacent to the film-substrate interface. In later work on strained LCMO films (grown on (001) SrTiO\(_3\)) they found evidence of localized Mn\(^{3+}\) and Mn\(^{4+}\) phases and of itinerant Mn\(^{3+/4+}\) phase. The presence of Mn\(^{3+}\) and Mn\(^{4+}\) localized states they associate with a FMI phase with A-type orbital ordering. On unstrained films (grown on (110) SrTiO\(_3\)) they only detected the itinerant Mn\(^{3+/4+}\) phase.\(^{96}\) Thus, the NMR data suggest that far below the MI transition, PS is absent or greatly diminished on the less-strained films. The insulating phase close to the interface would, with present knowledge, be connected to the effects of a charge discontinuity (the so-called polar discontinuity) at the LCMO/STO(001) interface.

Random telegraph noise (RTN) has been observed in resistance measurements of LCMO films. For manganites, this RTN will originate from fluctuations in the conductivity of electronic domains between metallic and insulating phases, or from fluctuations in the orientation of magnetic domains with associated fluctuations of interdomain resistance.\(^{97,98}\) Raquet et al studied the resistance noise of LCMO films.\(^{98}\) They detected RTN but only for \(T < T_c\). An applied magnetic field stabilized the low-resistance, ferromagnetic phase at the expense of the high-resistance phase but did not eliminate RTN. In fact RTN was present even at fields high enough to suppress magnetic domains. This suggests that although the low-resistance phase was magnetic—hence is was stabilized by a field—the noise was not magnetic in origin. Thus, they concluded, below \(T_c\), manganites consist of two phases, one a FM metal and the second a phase with reduced electronic and magnetic properties. In later analysis of similar LCMO films, other researchers concluded that low-temperature fluctuations were the result of magnetic domain orientation fluctuations and not from fluctuations between low and high resistance phases.\(^{99}\) They argued that since transport measurements indicated the film was metallic at the lowest temperatures, with no upturn in resistance at the very lowest temperatures, a picture of metallic phases embedded in an insulating matrix would not be plausible. This is because if the insulating phase made up a significant fraction of the film, then at low temperatures the increasing resistance of the insulating phase would come to dominate the decreasing resistance of the metallic phase. Instead they suggest that the fluctuating resistance of relatively thin domain walls separating FMM regions would provide sufficient re-
resistance to produce the RTN without coming to dominate the metallic phase at the lowest temperatures.

Measurements of electroresistance (ER) have also been used to investigate PS in manganite films.\textsuperscript{100,101} Relevant in this respect are data taken on microbridges of thin (10 nm) strained films of LCMO on STO.\textsuperscript{102} In these experiments it was found that the resistance of LCMO films depended upon the current used in the measurement, with higher currents leading to lower resistances, but only in a small temperature regime around the MI transition. When effects at lower temperatures were found, this seemed to be due to stronger disorder in those films, in line with reported data on films of La\textsubscript{0.8}Ca\textsubscript{0.2}MnO\textsubscript{3}, with a doping closer to the FI part of the doping phase diagram.\textsuperscript{103}

Summarizing, it appears that in homogeneous films the effects of PS are only to be expected (very) close to the MI transition. Strained films are more prone to disorder, and then also the metallic low temperature state can show PS. This can explain a variety of STM observations, but it does not yet explain why some of the data discussed here show the total absence of PS effects, even close to the MI transition.

### 3.4.2 Polarons and Pseudogaps

Several groups have measured LCMO films with STS and found them to be electronically homogeneous, and to have reproducible changes to dI/dV spectra with temperature. From these measurements they claim evidence of pseudogaps and polarons. In the context of STS, a pseudogap is generally defined as non-zero depletion of the DOS at the chemical potential ($\mu$).\textsuperscript{104} In contrast, a hard gap would have a range of energies about $\mu$ with a vanishing DOS. As was discussed above, JT polarons are expected in the PM phase, but whether they are present below $T_c$ remains controversial. In the discussion that follows, a somewhat artificial distinction will be made between pseudogaps and polarons. Pseudogaps will be defined as above, but polarons in STS data will be taken to mean a pseudogap or hard gap flanked by coherence peaks. The discussion begins with STS evidence of pseudogaps and continues with polarons.

#### Pseudogap

Pseudogaps have been observed on electronically homogeneous films by several researchers,\textsuperscript{83,89,105–107} describing their data in terms of a pseudogap width ($\Delta$) or a zero bias conductance (ZBC) or both. Mitra \textit{et al.}\textsuperscript{83} in particular, measured STS on atomically flat LCMO films grown on NGO. They observed that at temperatures close to $T_p$, a gap in the dI/dV spectra opens (maximum $\Delta \approx 0.6$ eV), which their analysis suggest is a depletion of the density of states. They extract ZBC (or $G_0$ in their notation) by fitting a power law function to the low bias part of numerically differentiated IV curves. Their plot of $G_0$ versus temperature is reproduced in Fig. 3.16 left. From the graph it is clear that the shape of the $G_0$-T curve is much like an inverted RT curve, with a variation in $G_0$ of about two orders
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Figure 3.16: (Left) Plot of $G_0$ (or ZBC) from Mitra et al.\textsuperscript{83} (Right) Plot of ZBC from Singh et al.\textsuperscript{107}

of magnitude. They measure conductance maps and claim them to be electronically homogeneous at all temperatures as a result of being grown on NGO. These findings certainly are compelling, and offer an explanation of the peak in resistance seen in transport measurements, without requiring PS.

Other research, though, does not find the same kind of behavior. Singh et al. found pseudogaps on flat but strained LCMO films at all measured temperatures.\textsuperscript{107} At 310 K the pseudogap was $\Delta \approx 0.25$ eV and increased—almost—monotonically to a 0.35 eV at 78 K, well below $T_c$. They also calculated ZBC. Their plot of ZBC versus temperature is shown in Fig. 3.16 right. Unlike Mitra et al, the ZBC does not drop significantly at $T_p$ (250 K) and in fact is approximately the same as at 310 K. Pseudogaps have also measured on electronically inhomogeneous films. Hughes et al. found pseudogaps in d$I$/d$V$ spectra measured at 300 K but found that the pseudogap varied across the sample surface.\textsuperscript{89} In the research reported here, the variation in ZBC on LCMO/NGO films varied little, ranging from between about $1.8 \times 10^{-11}$ to $5 \times 10^{-11}$ siemens, and showed no trend in temperature and no dip or peak at or near $T_p$ (see Fig. 3.9). At this time it is worth noting that all of the d$I$/d$V$ spectra displayed in Fig. 3.9 were measured with the same tunneling set-point. This was done in order to sidestep the difficulties that can be encountered in differentiating between the effects of changes in tunneling barrier—which the set-point can strongly influence—and changes to the sample DOS (see discussion of this issue in Sec. 2.7). Collectively, the evidence from pseudogaps is rather contradictory. This even though all of these measurements were made on similar films with similar bulk properties (magnetization and RT).
Figure 3.17: STS measurements on atomically smooth LCMO film grown on STO. (a) and (b) Plots of $I(V)$s measured at indicated temperatures. (c) Resistivity from transport measurement. (d) and (e) Normalized $dI/dV$s. Taken from Ref. 69

### Polaron-STS

That polarons are one part of the CMR model of LCMO manganites which is not controversial. In the paramagnetic phase, high temperature RT measurements are routinely fitted to a polaron model. Usually high temperature data best fits the small polaron (SP) model with resistivity 

$$\rho(T) \approx \rho_0 T^{\alpha} \exp\left(\frac{E_a(T)}{k_B T}\right)$$

where $E_a$ is the activation energy and $\alpha = 1$ for the adiabatic SP model and $\alpha = 3/2$ for the non-adiabatic SP model. Here the polaron binding energy, $E_b$, is twice $E_a$. Most papers report best-fit to the adiabatic SP, although there has been at least one report of best-fit to the non-adiabatic SP. Typical polaron binding energies range from 0.11 eV to 0.35 eV. Below $T_c$, in the metallic phase, the role of polarons has yet to be settled. Evidence of FM-phase polarons comes from both STS and other techniques.

Polarons have been claimed to exist in the STS spectra measured on manganite films. Seiro et al published electronically homogeneous STS measurements of a 31 nm thick strained LCMO film grown on STO. Again, this film was atomically flat with wide terraces separated by unit-cell step heights. They observe a gap flanked by coherence peaks in their normalized $dI/dV$ spectra, and claim this to be the signature of polarons, with half the peak-to-peak distance representing the polaron binding energy [see Fig. 3.17(d) and (e)]. They found that the binding energy varied with temperature, narrowing at temperatures close to $T_p$. This seems to be in conflict with transport measurements of their films that show the usual peak in resistance in this very temperature range [see Fig. 3.17(c)]. This contrasts with our results where
we see little evidence of polaron peaks. Shown in Fig. 3.18 are a representative set of normalized I-V curves for a 52 nm thick LCMO film on STO ($T_p$ 155 K), with similar doping and thickness to the sample studied by Seiro et al. A gap-like feature can be seen, but no peak-like features. The width of this gap (0.2 eV at half depth) is very similar to the values found by Seiro et al, but remains approximately fixed at temperatures above, below, or at $T_p$. Our results are not the only ones in conflict with Seiro et al. Normalized spectra measured on similar films by Singh et al do not have any obvious coherence peaks and the polaron binding energy—as estimated from the gap width—increases from 0.25 eV above $T_p$ to 0.35 eV well below $T_p$, without narrowing at $T_p$. In one of the first STS measurements of LCMO, Wei et al found evidence of polaron peaks (energy gap $\sim$0.5 eV) but only at 77 K, well below $T_c$. Above $T_c$ only a pseudogap, with no evidence of coherence peaks, was present in their normalized spectra. All of these measurements are from films that are claimed to be electronically homogeneous and with atomically flat surfaces. Further, although the nominal film Ca-doping is different for each report, the range of doping is narrow enough ($0.3 \leq x \leq 0.375$) to expect very similar behavior.

One issue may be that some data appear to be taken from only one sample. We found inconsistencies between our films grown under nominally identical process conditions, and found our conclusions to be more robust when drawn from a number of samples. Furthermore, some groups present example I-V curves that appear to be measured at different voltage set points. Considering the difficulty of separating sample DOS from the tunneling barrier, we would not want to draw conclusions from such a procedure and prefer to compare data taken at a single set-point, eliminating one source of uncertainty.†

3.4.3 Surface Effects

A number of studies have found that the surface of LCMO films does not have the same properties as the film bulk. This is critical for any surface-sensitive technique like STS. Since the STM tunneling current decreases exponentially with tunneling distance, just the film’s topmost conducting unit cell will directly contribute to the $dI/dV$ spectra. Only if the surface layer is electronically identical to the bulk will STS measurements probe the film’s bulk properties. There is reason to believe that the film surface may not have identical properties to the film bulk. Some researchers have detected dopant stratification through the film thickness, with the surface layer being either over- or under-doped. Other research has shown that the oxygen content at the film surface is very sensitive to elevated temperatures, whether in oxygen or UHV, or to prolonged air exposure. Finally, theoretical modeling suggests that crystal symmetry breaking due to the unavoidable truncation of the crystal by the film surface leads to non-bulk properties where the surface is frozen into an anti-ferromagnetic state. Because we did not directly measure the surface oxygen content at the film surface is very sensitive to elevated temperatures, whether in oxygen or UHV, or to prolonged air exposure. Finally, theoretical modeling suggests that crystal symmetry breaking due to the unavoidable truncation of the crystal by the film surface leads to non-bulk properties where the surface is frozen into an anti-ferromagnetic state.

†Singh et al make a similar point. They note that all of the IV curves they used to compute ZBC were taken with the same tunneling-gap resistance.
Figure 3.18: (Color online) Numerically differentiated and normalized $I$-$V$ curves of smooth 52 nm thick La$_{0.67}$Ca$_{0.33}$MnO$_3$ film grown on SrTiO$_3$ $T_p \approx 155$ K. $I_{set}=0.5$ nA, $V_{set}=0.5$ V, $V_{sweep} = \pm 0.5$ V. Measured in UHV at indicated temperatures with zero magnetic field.
or dopant concentration, we do not know if oxygen or dopant stoichiometry played any role in the inactive layer. However, without exception, we found that rough films—whether as-grown or roughened during oxygen annealing—were inhomogeneous, with an active surface, while flat films were homogeneous, with an inactive surface. This does provide support for crystal symmetry breaking as the cause of the inactive surface layer, though the exact mechanism is unclear.

With regard to the divergent results from STS measurements presented in the literature, one cause of this divergence could be the state of the film surface prior to measurement. Each group seems to have different way of preparing or preserving their film’s surface. These include no treatment (ours), isopropanol cleaning, rapid transfer to STM followed by rapid cool to low temperature, isopropanol cleaning followed by heating to 150 C in air. With regard to oxygen termination, one very recent publication can perhaps illustrate this issue. In this publication, Fuchigami et al performed STS measurements of an LCMO film grown and measured entirely in-situ. At room temperature, where transport measurements confirm the film bulk to be insulating, STS measurements of as-grown films prove to be metallic. However, after annealed in oxygen, a 1.35 eV bandgap opened up in the STS spectra. This process proved to be reversible—annealing in vacuum drove off the oxygen and the metallic, ungapped spectra returned.

3.5 Conclusion

We have used $dI/dV$ spectra calculated from STS $I-V$ measurements as a proxy for the surface DOS. With this method, we measured strained and unstrained LCMO films, and LCMO films with both flat and rough morphology. All of our flat films had inactive or ‘dead’ surface layers on otherwise active films. That is, we did not observe significant changes to $dI/dV$ spectra in response to either changes in temperature or applied magnetic field. However, transport and magnetization measurements of these films show typical MIT and CMR behavior, confirming that the film bulk was active. Rough films, on the other hand, whether grown on STO or NGO, had active surface layers. We find that the surface of these as-grown rough films responds to an externally applied magnetic field by becoming more metallic, as would be expected if percolation of metallic regions were to underlie CMR. On flat samples, we attempted to remove the inactive layer using ion etching. However, the post-etch $dI/dV$ spectra were not as expected and became more insulator-like at low temperatures, rather than metallic as would be expected from transport measurements. Possibly etching changed the surface stochiometry by preferentially etching one or more of the film’s chemical species. We oxygen-annealed other flat films to rule out oxygen deficiency as cause of the inactive layer. Unfortunately, annealing roughened the surface, rendering a direct comparison with pre-annealing flat samples questionable. STS and conductance maps of these annealed—and now roughened—films showed them to be electronically inhomogeneous. Strain does not seem to play a direct role in the for-
mation of the inactive surface layer as results from LCMO films grown on NGO and STO were very similar.

The body of evidence for phase separation phenomena from STS measurements in the literature is conflicting. Electronic PS has been detected on both rough\textsuperscript{66,67} and smooth\textsuperscript{89,90,93} films, while electronic homogeneity has only been detected on smooth films,\textsuperscript{69,83} never on rough films. The evidence from MFM measurements are no more conclusive. While one report found evidence of mixed FM and COI phases below $T_c$,\textsuperscript{70} another report on a similar sample found only a homogeneously distributed FM phase.\textsuperscript{92}

Evidence of polarons in the FMM phase of LCMO has come from both STS and other, less surface-sensitive techniques. In STS spectra, the evidence of polarons is taken to be either a gap or pseudogap flanked by coherence peaks,\textsuperscript{69,82} or even a pseudogap without coherence peaks.\textsuperscript{107} Taking only those publications that explicitly claim to observe polarons, the evidence for polarons in the FMM phase is contradictory. In one publication STS spectra only contain coherence peaks at low temperatures,\textsuperscript{82} while in another coherence peaks are a fixture at all temperatures.\textsuperscript{69} Finally in a third, there are no coherence peaks at any temperature, though a pseudogap—evidence they claim of polarons—is present at all temperatures.\textsuperscript{107} In our measurements we observed a pseudogap in STS measurements of our electronically homogeneous films, but did not observe coherence peaks. Optical conductivity measurements indicate the presence of polarons in the FMM phase, though there is some disagreement about whether they are large or small polarons. Other measurements—EXAFS,\textsuperscript{119} isotope-effect,\textsuperscript{120} and at least one resistivity measurement\textsuperscript{121}—generally support the existence of polarons below $T_c$.

There is little consistency in the polaron binding energy either. In STS work, the polaron binding energy is typically measured by either half the peak-to-peak width,\textsuperscript{69} or the gap width at half depth.\textsuperscript{107} One group measured an almost monotonic increase in binding energy with decreasing temperature,\textsuperscript{107} while another group saw an overall decrease in binding energy with decreasing temperature, but with a significant drop in polaron binding energy at $T_c$.\textsuperscript{69} In comparison, binding energy extracted optical conductivity increased monotonically with temperature until plateauing above $T_c$.\textsuperscript{122}

The best summary which can probably be made is that, depending on the disorder in the sample, the low-temperature metallic state can show more or less signs of phase separation. STM data certainly have caught such samples. When the disorder is low, PS phenomena only play a role in a very narrow temperature regime just below $T_p$, though this has never been clearly observed in STS. Compounding the difficulty here is that films with very smooth surfaces are probably electronically inactive—or at the very least, electronically different—because of symmetry breaking at the surface. This then precludes direct observation of what happens in the bulk.