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Complex oxides studied by Scanning Tunneling Microscopy / Spectroscopy

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Microscopy/Spectroscopy

Simon Kelly

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For Amity

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Chapter 1

Introduction

This thesis represents a series of measurements where the connecting theme is the use of scanning tunneling spectroscopy (STS) to measure the spatial distribution of the density of states (DOS) of various samples in materials where electron correlations play a role in various ways. Attention is focused on thin film oxides where the Mott insulating state is converted to a metallic one by doping; and on a superconductor / ferromagnet hybrid where the superconducting correlations were studied which were induced in the ferromagnetic film. The oxides were based on manganite and cobaltate perovskites

A scanning tunneling microscope (STM) is used in this thesis to measure both topography and the local density of states (LDOS). One of the properties of tunneling is that the LDOS can be estimated by differentiating a sweep of current (I) versus voltage (V). This is the differential conductance (dI/dV). Two types of tunneling junctions are commonly used to measure tunneling conductance in correlated electron systems and superconductors: planar junctions and STM's. While planar junctions are capable of very high energy-resolution and are thermally very stable, they measure the density of states averaged over the whole junction area. STM, on the other hand, offers the capability to map the sample *local* density of states with nanometer or finer resolution. Further details of STM and STS are discussed in Chapter 2.

STS measurements of manganites at varying temperatures and in varying applied magnetic field are discussed in Chapter 3. The manganites studied here are thin-film perovskite manganites with the chemical formula, $RE_{1-x}A_x\text{MnO}_3$, where RE is a trivalent rare earth (La, Nd, Pr) and A is a divalent alkali (Sr, Ca, Ba). Manganites are perhaps best known for a very large or colossal magneto-resistance (CMR). Magnetoresistance is characterized as a change in resistance brought about by the application of an external magnetic field. In some doped manganites, in particular those doped with La and Ca, the magnetoresistance has been measured with values up to 1000% or more.¹ The ground state of manganites depends upon the particular dopants and doping level and includes ferromagnetic, antiferromagnetic, and charge ordered states, amongst others. These materials are typically paramagnetic above a dopant-dependent Curie temperature (T_c). In this work, a La and Ca doped manganite, $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$, with doping $x = 0.33$ is studied (henceforth designated LCMO). At this doping level, LCMO is paramagnetic at temperatures above T_c while ferro-

magnetic below. This doping level was chosen because it has close to the highest T_c . Because of its high T_c , LCMO with $x \sim 0.33$ is often referred to as optimally doped. At temperature close to T_c , LCMO will undergo a metal-insulator (MI) transition coupled to the magnetic transition. Above the transition temperature (T_{MI}), LCMO is insulating, while below T_{MI} it is metallic. One outstanding issues with manganites is a complete understanding of the electronic properties of the metallic ground state which is formed below the MI transition. One issue here is the electronic phase separation, its underlying driving mechanism, and its spatial extent. In this picture, particularly at temperatures close to T_c or T_{MI} , both metallic and insulating phases are expected to be present. Both colossal magnetoresistance and the metal-insulator transition are explained as the percolation of the metallic phase producing conducting pathways throughout the material. In an applied field, the metallic regions will enlarge and subsequently coalesce into metallic pathways. Similarly, as the sample temperature is dropped below T_{MI} , the metallic regions will also grow and produce conductive pathways. In this Chapter the electronic phase separation is investigated in thin-film LCMO using STS. Measurements were conducted on both rough and atomically smooth films. These measurements show that the surface morphology plays a key role in determining whether phase separation is detectable with STM, with phase separation being detected on rough films but not detected on smooth films. In addition, an electronically dead layer was present on the smooth films that was not present on rough films.

STS measurements of thin-film cobaltites are discussed in Chapter 4. The particular cobaltite studied here is $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$. This material has a perovskite crystal structure like the $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$ studied in Chapter 3. While $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ is magnetoresistive like LCMO, both the magnitude and the underlying mechanism is different. At most doping levels, the $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ magnetoresistance is limited to a few percent, though it does reach as high as about 100% for low doping ($x \sim 0.09$) and low temperatures ($T < 50$ K). The mechanism of magnetoresistance in $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ for $x < 0.18$ is thought to be giant magnetoresistance-like, with ferromagnetic (F) clusters embedded in a non-ferromagnetic matrix. In this model, the giant magnetoresistance comes about from the external field aligning adjacent ferromagnetic-clusters and thus enhancing cluster-to-cluster transport. In bulk form, the ground state is a cluster-ferromagnet for doping $x > 0.18$, but becomes a spin glass for $x < 0.18$. In the low doping, spin glass phase, inhomogeneities have been found in bulk cobaltites. At much higher doping, no evidence of inhomogeneities has been found. In contrast, even with doping as high as $x = 0.5$, inhomogeneities have been detected on films thinner than a critical thickness (t^*). In this Chapter, the inhomogeneity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ films both thicker and thinner than t^* will be explored using STS to map the conductance. In agreement with other published measurements, films thinner than t^* were electronically phase separated while films thicker than t^* were electronically homogeneous.

In Chapter 5 the local density of states (LDOS) at the surface of the ferromagnetic layer of a ferromagnetic/superconductor (FS) bilayer is presented. When a non-superconducting or normal (N) metal is in good electrical contact with a super-

conductor (S), Cooper pairs will leak from the S into the N metal. These Cooper pairs produce changes to the DOS in the N metal. This is the proximity effect. One way to detect these Cooper pairs is to measure the LDOS at the surface of the normal metal. This can be done with planar tunneling junctions or an STM. The characteristic feature of the proximity effect in a non-magnetic N metal is a gap at the Fermi energy with magnitude on the order of the S-layer gap width. The depth of this gap, though, is proportional to the order parameter (OP) induced in the N-metal. In a non-ferromagnetic N-metal, the OP will decay as a function of the distance from the S-N interface. If, however, the N-metal is ferromagnetic, then the OP will oscillate as well as decay. Because of this oscillation, the OP in a ferromagnet can even be negative, meaning that the phase has now changed by π . While the OP is positive, the LDOS will be gapped. This is labeled the zero state. In the π state, the LDOS gap will be inverted. Because tunneling is surface sensitive and only measures the LDOS at the vacuum- or insulator-sample interface, the thickness of non-superconductor layer (d) must be varied in order to observe the zero and π states. Typically this is done by growing a series of bilayers with varying d . In this work, variations in the the LDOS are explored by measuring an FS bilayer where the film roughness has produced lateral variations in d . Variations in LDOS were indeed observed on the film but they were not consistent with an estimate of the F-layer thickness derived from a model fit to the spectra. Some spectra were measured with an inverted LDOS, but these spectra were not consistent with the shape of inverted DOS measured by other researchers or predicted by theory.

Chapter 2

Scanning Tunneling Microscopy/Spectroscopy

2.1 Introduction

Scanning Tunneling Microscopy (STM) was the principal tool used for gathering data in this Thesis. As such, a basic description of STM and an introduction to the basic function, basic components, and underlying theory will demonstrate both the advantages and disadvantages of this tool.

STM was used to measure both topography and spectroscopy. Ideally, STM topography maps the position of surface atom cores, and scanning tunneling spectroscopy (STS) measures the local density of states (LDOS) of the sample. As measuring the LDOS is the focus of this research, STS was of primary interest. But because surface topography and the sample LDOS can be strongly correlated, STS was only performed in conjunction with STM topographic measurements.

Spectroscopy, though, is not without difficulties. In its favor, and the most important reason STS is used to measure LDOS, is that STS affords very fine spatial resolution, at the level of single molecules² or even single atoms.^{3,4} The primary difficulty with STS is that tunneling spectra are always a convolution of sample DOS, tip DOS, and the highly non-linear tunneling barrier. Separating the sample DOS from tunneling spectra is non-trivial and more will be said about this later. Compounding this, as tunneling is limited to within angstrom of the sample surface, tunneling spectra can be dominated by surface electronic structure. If a measurement of the surface electronic structure is desired, then STS is an ideal tool, but for bulk DOS some effort must be made to verify that what is measured is bulk and not surface DOS.

The rest of this Chapter is organized as follows. Immediately following this introduction, some specific details of the STM's used in this study are presented (Sec. 2.2). This is followed by a general introduction to the STM (Sec. 2.3), and then, in greater detail, a discussion of piezoelectric actuators (Sec. 2.4), and technical issues surrounding measuring the tunneling current (Sec. 2.5). This is followed by discussions of implementing STM topography (Sec. 2.6), STS (Sec. 2.7) and details of the

theory behind STS (Sec. 2.8).

2.2 STM Instruments and Techniques Used in this Study

The measurements in this Thesis were made almost exclusively with STM's designed and built within the group. Other measurements were made with commercial STM's but these were used only to verify measurements already made using self-made instruments. These two STM's were a flow-cryostat STM and a UHV STM. The flow cryostat and UHV STM's are similar and are both based upon the Pan design.⁵

The UHV STM consists of a home made microscope and UHV chambers connected to a Heliox^{UHV} ^3He refrigerator from Oxford Instruments. The ^3He refrigerator is a one-shot type⁶ meaning that the ^3He must be recondensed after each cooling cycle, limiting the base temperature hold-time to about 25 hours under the STM heat-load. The STM is suspended by a spring from the refrigerator and both are fitted inside the UHV tube.

The UHV tube is surrounded by a cryostat containing about 70 liters of liquid helium used to cool the superconducting magnet (10 T, parallel to STM vertical axis, perpendicular to the sample surface) and for the ^3He refrigerator operation. The practical liquid helium hold time, without warming up the superconducting magnet, is about 60 hours.

The Heliox^{UHV} refrigerator is especially developed for STMs in UHV, which has a number of consequences for its design: the refrigerator itself has been designed to be not extremely rigid, in order to isolate from external mechanical and acoustic noise. The UHV environment does not allow for use of ^4He exchange gas for first cooldown, therefore the ^3He inside the refrigerator is used for this purpose. Finally, to allow in situ tip/sample exchange, part of the refrigerator can be elongated with a vertical lead screw; for this reason the ^3He and ^4He capillaries are in large part coiled up to allow extension. When the refrigerator is in fully retracted position [as in Fig. 2.1(a)], the STM is freely suspended in the middle of the superconducting magnet (measurement position). When the refrigerator is in the fully elongated position (insert extends about 50 cm down into the UHV chamber) tip and/or sample can be reached and exchanged with a mechanical hand.

This low temperature STM is designed for best performance in a temperature range between 300 mK and 2.5 K. Nevertheless, by using a heater installed on the ^3He pot, the STM can also operate at temperatures up to 180 K, although cooling and warming cycles are very slow in this "high-temperature" mode. The temperature was measured with CernoxTM CX-1030 thermometer calibrated by the manufacturer, Lake Shore Cryotronics, Inc., and mounted on the STM close to the sample. Because the thermometer was not attached directly to the sample, the sample and the thermometer temperatures can differ. This difference can be estimated by measuring a superconducting gap and fitting this gap using a thermally-smeared BCS density of states, with the effective sample temperature typically about ~ 450 mK warmer

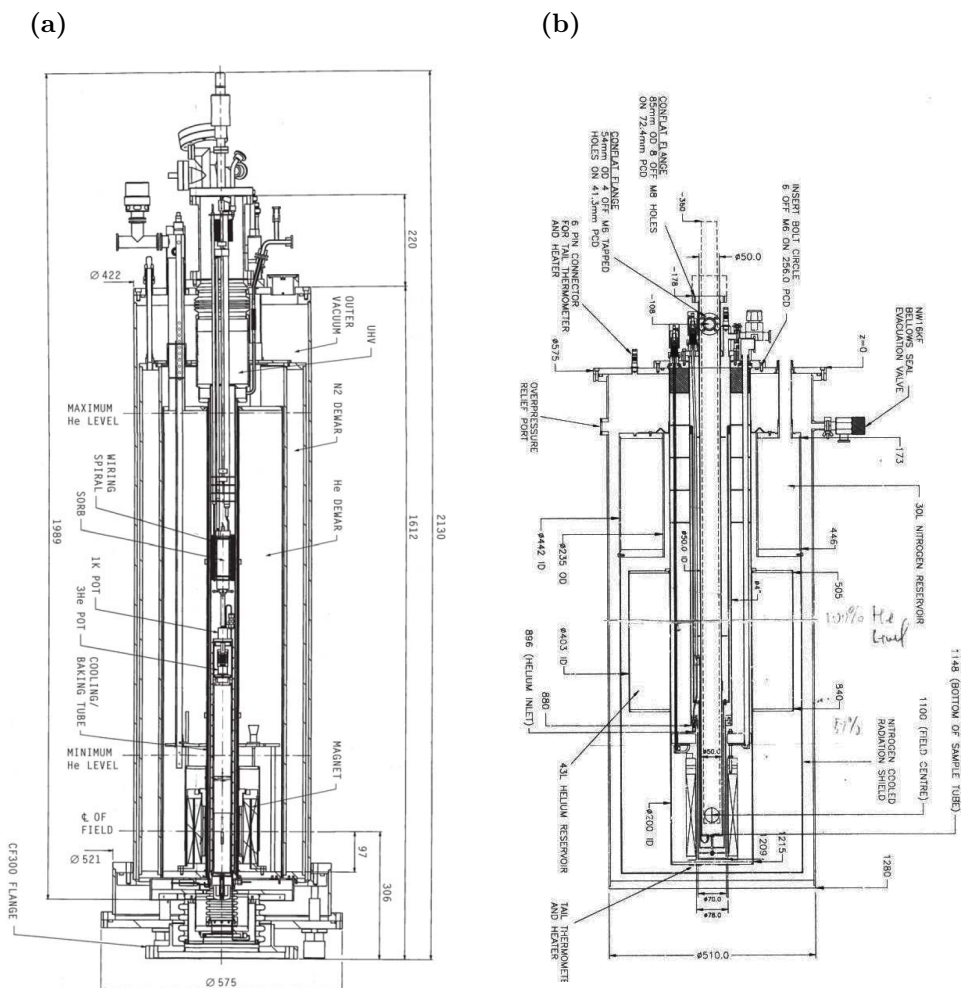


Figure 2.1: (a) Cross-section of UHV Cryostat. (b) Cross-section of VTI Cryostat. See text for further details.

than the thermometer reading at ~ 1 K. An example fitted Nb superconducting gap is shown in Ch. 5. The bottom of the cryostat is connected to a Leiden-designed UHV chamber which is pumped by a 300 liters/s ion pump, a titanium sublimation pump, or both. The UHV tube is protected from thermal radiation emanating from the UHV chamber with a liquid nitrogen cooled shield, which opens when the STM is lowered into the UHV chamber. The UHV chamber contains tip/sample storage plus leak-valves and evaporation cells for tip/sample preparation.

Samples and tips are loaded into the main UHV chamber via a hybrid load-

lock/preparation chamber. This chamber is evacuated with a 200 l/s turbo pump that is also used for initial, pre-bake system pump-down. For surface and tip cleaning and annealing the load-lock is equipped with a 0.2-5 kV ion-source and a heating stage.

The entire STM is suspended on air-dampers (Kinetic Systems Inc.), which rest on a heavy concrete island further isolated from the rest of the laboratory.

The STM head has been designed and built in Leiden by S. Otte.⁷ The Z-approach and Z-scan mechanisms are integrated in one single piezo-motor based on the Pan design, and the XY motion is done with a XY-shear piezo stack to increase the mechanical resonance frequency and decrease the mechanical loop. The STM is connected to two stainless steel coaxial cables for tunneling current and bias ($R = 120 \, \Omega$ and $C = 1.2 \, \text{nF}$ each) and 5 non-shielded stainless steel thin wires for driving the piezos. The STM feedback and scanning is done with a commercial controller (RHK Technology Inc. SPM 1000) and the current is amplified either by a RHK pre-amplifier at fixed gain ($10^9 \, \text{V/A}$) or a Femto GmbH pre-amplifier at variable gain. Both amplifiers have comparable noise level of about $0.2 \, \text{pA}/\sqrt{\text{Hz}}$ with the above mentioned sensitivity and the input impedance of the wires. The STM has a XY-range of $300 \, \text{nm} \times 300 \, \text{nm}$ at base temperature and about 5 times more at room temperature. The STM is lateral and vertical stable to about $0.2 \, \text{\AA}$ in 30 minutes.

Even though the STM is suspended on air-dampers and relatively isolated inside the UHV chamber, intermittent external mechanical and acoustic noise sources were able to couple into the tunneling signal at times. Particularly 2 and 11 Hz from the eigen-frequency of the air-dampers and $\sim 20\text{--}24 \, \text{Hz}$ from the air-conditioning system of the laboratory. The first can be reduced by improving the damping of the air-pillars, but the latter would require a full acoustic isolation of the entire setup.

The exchange-gas STM is a home made STM in helium boil-off gas within a variable temperature insert (VTI) from Cryogenic Ltd (see Fig. 2.1) mounted through the bore of a 12 T magnet. Using resistance heating, the sample temperature can be varied between 4.2 K 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. The cryostat was initially suspended with 3 springs on the laboratory ceiling but in a later stage mounted in a heavy frame (stainless steel filled with sand) on top of air-dampers from Newport. The STM head was designed and built in Leiden.⁸ The coarse-approach is based on the standard Pan design, and it can be used either as slip-stick or walker (the latter more reliable at low temperatures). This STM offers more XYZ range ($2 \, \mu\text{m}$ at 300 K, 5 times less at 4 K) because it is based on a piezo-tube scanner. Tip and samples cannot be changed in situ. The noise level is somewhat better than for the UHV STM because of the lower input impedance of the wires. The STM is suspended at the end of a relatively floppy insert (resonant frequency about 200 Hz) with a spring of lower frequency $\sim 100 \, \text{Hz}$. Also this STM was affected intermittently by acoustic noise from the laboratory

ventilation system. The same type of electronic was used as for the UHV STM.

One issue common to both the flow-cryostat STM and the UHV STM is the length of the coaxial cable connecting the STM to the transimpedance amplifier used to measure the tunneling current. This is a problem because the capacitance of a coaxial cable is proportional to its length (~ 100 pF/m)[†] and increasing the input capacitance of the transimpedance amplifier, as will be discussed in more detail below, will increase its noise floor. Unfortunately, the length of the coaxial cable was driven by the need to cool the STM to cryogenic temperatures and a concomitant requirement for thermal isolation.[‡]

Both mechanically cut PtIr (90%:10%) and electrochemically etched Pt wires were used as STM tips. No significant difference between these two types of tips was apparent.

2.3 Basic STM Function

The STM tip-sample distance can be controlled with sub-nanometer resolution because of the exponential dependence of tunneling current on tip-sample distance. The tunneling current (I_{tunnel}) as a function of tip-sample separation (z) can be written,⁹

$$I_{\text{tunnel}} \propto e^{-2\kappa z}, \quad (2.1)$$

where

$$\kappa^2 = 2m\bar{\Phi}/\hbar^2, \quad (2.2)$$

and where $\bar{\Phi}$ is the average work function, and m the electron mass. Using a typical value for the work function, 5 eV, the tunneling current will change by an order of magnitude for every 1 Å change in the barrier thickness.⁹

In order to operate, the STM tip and sample must first be close enough for electrons to tunnel between them but not so close as to be in contact. This is usually accomplished with a combination of coarse approach and fine-control mechanisms. Typical coarse approaches are capable of motion on the order of millimeters. Within a micron of the surface, the fine control will take over. A schematic showing the basic components of an STM is shown in Fig. 2.2. In this Figure, the tip is mounted onto a piezoelectric tube—fine-control—which itself is mounted onto the coarse approach mechanism. This is the configuration the flow-cryostat and UHV STM's used in this research. Many other arrangements are possible. Much more will be said about both the coarse and fine control mechanisms later in this Chapter.

Operation of an STM begins with the tip and sample separated by a distance on the order of millimeters, which allows the tip or sample to be changed without

[†]One STM used in this research used Lakeshore Cryogenics, Inc. Type C coaxial cable with a capacitance of 79 pF/m.

[‡]The coaxial cables for the flow-cryostat STM and the UHV STM were ~ 1 m and ~ 5 m, respectively.

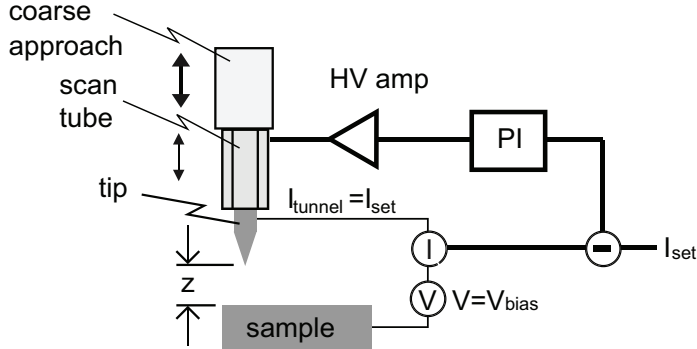


Figure 2.2: Basic STM components plus feedback loop. Adapted from Ref. 10.

damaging either of them. A fixed bias voltage (V_{bias}) is then applied between the tip and sample. The tunneling current between the tip and the sample is measured by a transimpedance amplifier. With an initial tip-sample separation of millimeters, there will be no detectable current. The tip and sample are then brought together slowly by stepping the coarse approach. Each step of a typical STM coarse approach will consist of retracting the fine-control mechanism, stepping the coarse mechanism, and then extending the fine-control mechanism while testing for a tunneling current. This cycle is repeated until I_{tunnel} rises to the current set-point (I_{set}). Once the coarse approach has halted, a feedback mechanism will assume control of the tip-sample separation.

The purpose of the STM feedback mechanism is to maintain tunneling current set-point by adjusting the tip-sample distance with the fine-control mechanism, usually a piezoelectric actuator. This feedback mechanism is needed because the tip-sample distance can change because of changes in the sample topography as the tip is scanned laterally, due to thermal drift, or other errors such as piezoelectric creep. At the heart of the feedback mechanism is an analog or digital proportional-integral or PI controller and a high-voltage (HV) amplifier. The PI controller adjusts the tip-sample distance in response to any difference between I_{tunnel} and I_{set} . If $I_{tunnel} < (>) I_{set}$, then the PI controller will decrease (increase) z using the fine-control mechanism causing an increase (decrease) in I_{tunnel} until $I_{tunnel} = I_{set}$. The HV amplifier is necessary because the strain coefficient of the piezoelectric materials used in the fine-control mechanism is small, requiring a large field to produce any appreciable motion. Due to the exponential dependence of I_{tunnel} on z , small changes in z will generate large changes in I_{tunnel} [see Eq. (2.1)]. It is this sensitivity and the small strain coefficient of piezoelectric materials that permits the PI controller to effectively control the tip to within Å's of the surface.¹⁰

The final component needed for a functioning STM is a way to scan the tip laterally across the sample surface. In the design described above, a piezoelectric tube will provide this function. In one STM used in this research, scanning was accomplished

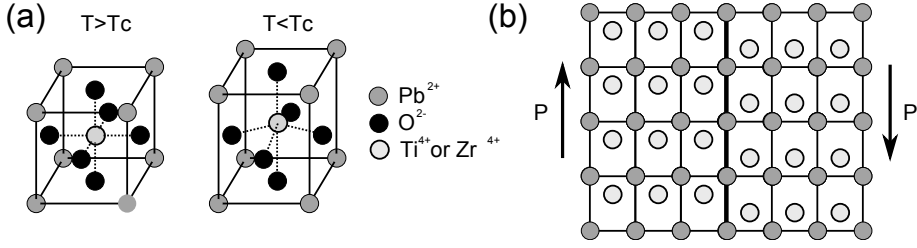


Figure 2.3: (a) Structure of PZT is cubic above T_c and tetragonal below. (b) Domain structure of PZT in tetragonal/ferroelectric phase. Adapted from Refs. 12,13

with an actuator comprised of two shear piezoelectric actuators, stacked one on top of the other, with their shearing motions directed orthogonally. Other arrangements are possible.¹¹

2.4 Piezoelectric Actuators

In this research, all of the STMs used piezoelectric actuators for the fine-control, scan, and coarse approach functions. Because of this, an introduction to piezoelectricity and piezoelectric actuators, including a discussion of their advantages and disadvantages follows.

2.4.1 Basics of Piezoelectric Materials

Piezoelectric materials are commonly used for STM actuators. The most common material is PZT (lead zirconate titanate, $Pb[Zr_xTi_{1-x}]O_3$). Among the advantages of piezoelectric materials, and in particular PZT, are that they have high sensitivity (on the order of 10 nm motion per applied volt); that they can be made UHV compatible (minimal outgassing, bakeable); that they do not generate nor are they affected by magnetic fields; and that they can operate at temperatures from mK to well above room temperature. PZT is a solid solution of two perovskites, $PbTiO_3$ and $PbZrO_3$, with mixtures of containing roughly equal parts of Ti and Zr showing the largest piezoelectric strain coefficients (see below).¹²

The structure of PZT is shown in Fig. 2.3(a). Above the Curie temperature (T_c) PZT is cubic and paraelectric, but below T_c it is tetragonal and ferroelectric. To form the tetragonal structure, four of the Pb^{2+} ions will shift along, what is designated, the c-axis, elongating the unit cell. Simultaneously, the Ti^{4+} or Zr^{4+} ion, formerly at the center of the unit cell, will be displaced along the same axis, and together with the O^{2-} ions, this will create a ferroelectric dipole parallel to the c-axis. Because the elastic energy will favor adjacent unit cells having parallel c-axes, domains will form with parallel dipoles. However, because this polarization will also create a surface charge with its associated depolarization field, large domains will break up into

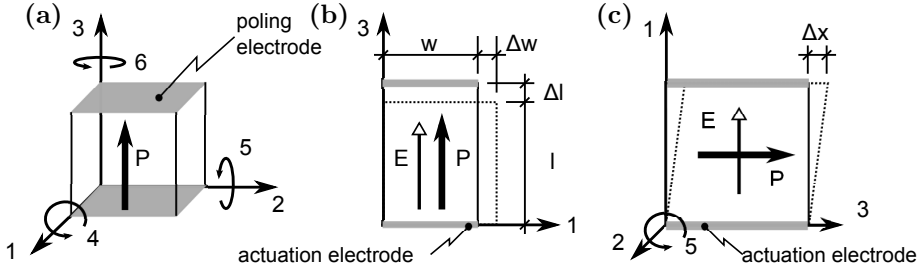


Figure 2.4: Relationship between poling axis, applied field, and actuation. (a) The axes are defined in relation to the poling axis. (b) A field applied parallel to poling axis will cause both a parallel and a perpendicular response. (c) A field applied perpendicular to the poling axis will cause shearing parallel to the poling axis. Adapted from Ref. 12

smaller domains with anti-parallel polarization [see Fig. 2.3(b)].¹³ Defects and strain will cause further domain generation, resulting in domains with randomly oriented polarizations. Given this and that commercial PZT is polycrystalline, virgin PZT will have no net polarization. To be useful, PZT must be poled in a high electric field at, possibly, an elevated temperature to reorient the domains in one predominant direction.^{12,14,15} PZT is ferroelectric and, therefore, a piezoelectric material. This is true of all ferroelectrics. A piezoelectric material, however, need not be ferroelectric. Quartz is a prominent example of a non-ferroelectric piezoelectric.

The piezoelectric effect is the generation of an electric field in response to strain. Piezoelectric actuators rely on the inverse piezoelectric effect, where an applied electric field induces strain. For the inverse piezoelectric effect in one-dimension, the strain (S) is related to the applied field (E) by,

$$S = d_1 E, \quad (2.3)$$

with the piezoelectric constant, d_1 , in unit of meters per volt. At constant stress T (the force per unit area), this constant is defined by,

$$d_1 = \left(\frac{\partial S}{\partial E} \right)_T. \quad (2.4)$$

In general, a piezoelectric material will also be subject to stress, and so, in three-dimensions, the equation of state relating the inverse piezoelectric and elastic strain is given by,

$$\mathbf{S} = \mathbf{s}^E \mathbf{T} + \mathbf{d} \mathbf{E}, \quad (2.5)$$

where $\mathbf{S}$ and $\mathbf{T}$ are now tensors, $\mathbf{d}$ is a matrix, and $\mathbf{s}^E$ is the elastic compliance matrix defined in constant electric field.¹²

The actuation direction of a piezoelectric is determined by the relationship between the poling axis (P) and the electric field axis. When $E \parallel P$, the material responds by straining both parallel and perpendicular to the field axis [Fig. 2.4(b)]. When $E \perp P$, the material responds by shearing perpendicular to the field axis [Fig. 2.4(c)]. The directions of a piezoelectric are labeled 1, 2, and 3, forming a right-handed orthogonal coordinate system [Fig. 2.4(a)]. By convention, axis 3 denotes the poling direction. The piezoelectric properties are given in relation to this coordinate system. The strain coefficient (d_{ij} [m/V]) gives the strain in direction- j with a field applied in direction- i . For STM actuators, the d_{33} (parallel), d_{31} (perpendicular), and d_{15} (shear) coefficients are the most important. Writing Eq. 2.5 explicitly,¹²

$$\begin{bmatrix} S_{11} \\ S_{22} \\ S_{33} \\ 2S_{23} \\ 2S_{31} \\ 2S_{12} \end{bmatrix} = \begin{bmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ s_{21} & s_{22} & s_{23} & 0 & 0 & 0 \\ s_{31} & s_{32} & s_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{66} \end{bmatrix} \begin{bmatrix} T_{11} \\ T_{22} \\ T_{33} \\ T_{23} \\ T_{31} \\ T_{12} \end{bmatrix} + \begin{bmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{32} \\ 0 & 0 & d_{33} \\ 0 & d_{15} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \quad (2.6)$$

This equation can be considerably simplified if the piezoelectric is unconstrained and not subject to external stress ($T_i = 0$). Then for an applied field E_3 only (which means $E \parallel P$), Eq. 2.6 will reduce to,

$$S_{11} = d_{31}E_3 \text{ and } S_{22} = d_{32}E_3, \quad (2.7)$$

which is a strain along both axes perpendicular to the applied field, and

$$S_{33} = d_{33}E_3, \quad (2.8)$$

a strain along the same axis as the applied field. Similarly, if a field is applied along axis 1, E_1 , then the piezoelectric will shear. From Eq. 2.6,

$$\gamma = 2S_{31} = d_{15}E_1, \quad (2.9)$$

where γ is the total shear strain.

Equations 2.7 through 2.9 can be rewritten in terms of applied voltage, V , and the piezoelectric dimensions. If V is applied across a piezoelectric of length l and in the same direction as the poling direction, then the displacement parallel to the field is,

$$\Delta l = d_{33} \left(\frac{V}{l} \right) l, \quad (2.10)$$

while the displacement perpendicular to the field is,

$$\Delta w = d_{31} \left(\frac{V}{l} \right) w. \quad (2.11)$$

Similarly, when potential V is applied across a piezoelectric of length l , but perpendicular to the poling direction, the piezoelectric will shear, with the total shear given by,

$$\Delta x = d_{15} \left(\frac{V}{l} \right) w. \quad (2.12)$$

Piezoelectric materials can also generate a force. For a field applied along axis 3, consider only the strain along axis 1 and ignore the strain along axis 3. In this case, Eq. 2.6 will reduce to,

$$S_{11} = s_{11}T_{11} + d_{31}E_3. \quad (2.13)$$

This is Eq. 2.7 generalized to include an additional term, $s_{11}T_{11}$, accounting for any force applied to the piezoelectric along axis 1. This could be an externally applied force, or the force generated as the piezoelectric attempts to expand, contract, or shear against a constraint. Consider a simplified case of a piezoelectric material contained within perfectly rigid constraint along axis 1. This constraint is the same length as the piezoelectric before the field is applied so it will initially be unstrained. Because of the constraint, though, the piezoelectric cannot expand or contract along axis 1. This means that $S_{11} = 0$ and Eq. 2.13 can be rewritten as,

$$T_{11} = -d_{31}E_3/s_{11}, \quad (2.14)$$

where T_{11} is the stress (or force per unit cross-section) generated. The force generated is simply the stress multiplied by the cross-sectional area perpendicular to axis 1,

$$F = A_1T_{11} = -A_1d_{31}E_3/s_{11}. \quad (2.15)$$

This is the maximum force a piezoelectric can generate for a particular applied field. Piezoelectric actuator manufacturers will often list a blocking force as one of an actuators specifications. The blocking force is the maximum force that a piezoelectric actuator can generate at the maximum rated voltage. Increasing the voltage above the rated maximum will in principle increase the maximum force, but doing so will reduced actuator lifetime, and at high enough field cause dielectric breakdown. Operating the actuator at less than the maximum rated voltage will result in a blocking force less than the maximum. As can be seen from Eq. 2.15, the blocking force is linear in applied field.

Similar equations can be found for shear piezoelectrics. The shear strain for a piezoelectric with a field applied along axis 1 will be,

$$\gamma = 2S_{31} = s_{55}T_{31} + d_{15}E_1. \quad (2.16)$$

Now consider the same shear piezoelectric without an externally applied stress but with a perfectly rigid constraint resisting the piezoelectric from shearing. This will mean that $\gamma = S_{31} = 0$, and Eq. 2.16 will be reduced to,

$$T_{31} = -d_{15}E_1/s_{55}. \quad (2.17)$$

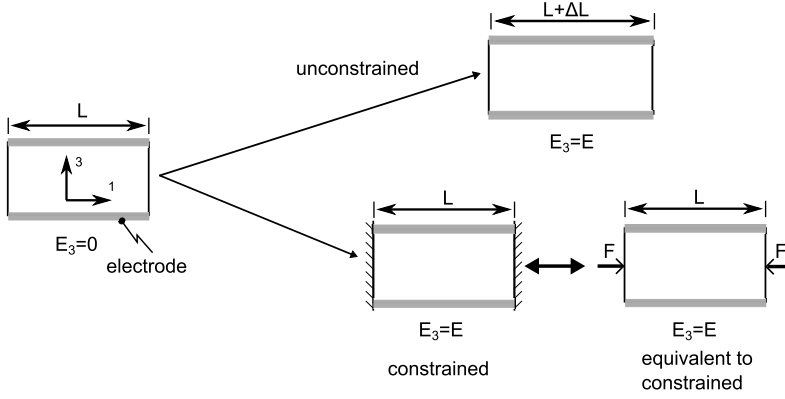


Figure 2.5: Piezoelectric unconstrained (giving rise to a change in the length L); or constrained along axis 1 with electric field applied along axis 3.

This is the shear stress that will be felt by the constraint. The force generated is just the shear stress scaled by the cross-sectional area of the piezoelectric perpendicular to the poling direction,

$$F = A_3 T_{31} = -A_3 d_{15} E_1 / s_{55}. \quad (2.18)$$

The forces that piezoelectric actuators generate can be understood in a different but equivalent way by comparing a piezoelectric without constraint to the same piezoelectric with constraint. Consider the piezoelectric shown in Fig. 2.5. Before E_3 is applied, the piezoelectric has length l . After the field is applied, the unconstrained piezoelectric will have expanded by Δl along the 1-axis, while the constrained piezoelectric will remain the same length.[†] Viewed from an alternate but equivalent prospective, consider the force needed to compress the unconstrained piezoelectric of length $l + \Delta l$ down to length l . For a small strain and within the elastic range of a material, the force required to uni-axially compress a body is given by Hooke's Law, $F = EA\Delta l / (l + \Delta l)$, where E is the elastic modulus of the material and A is the area perpendicular to the strain. PZT, the piezoelectric material used in most STM actuators, is an approximately Hookean material, and so this equation applies. This force is exactly the same as the force that the constrained piezoelectric will impose on the constraints.

2.4.2 Scan Tube

Topography is typically measured by scanning a tip over surface a while the feedback loop adjusts z to maintain $I_{tunnel} = I_{set}$. For this a method of moving laterally is

[†]This is true for a perfectly rigid constraint. If the constraint is compliant, the piezoelectric will lengthen to some degree, and the force imposed on the constraint by the piezoelectric will be less than that for a perfectly rigid constraint.

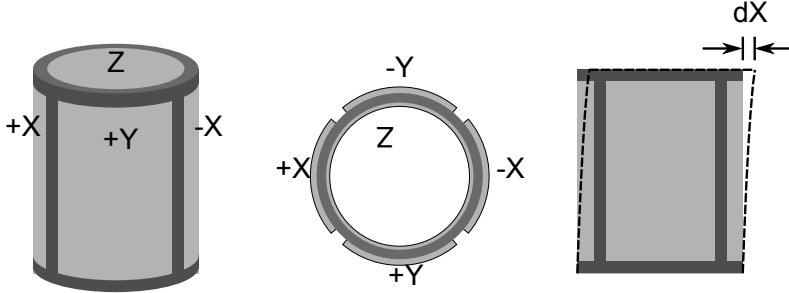


Figure 2.6: 5-Electrode Scan Tube.

needed. This is usually accomplished with one or more piezoelectric actuators. A common configuration, and one that has been used since the early days of STM,¹⁶ is a single piezoelectric tube with one electrode on the inner surface and four electrodes on the outer surface (Fig. 2.6). If poled radially, this single, 5-electrode tube is sufficient provide 3-axis motion.

For z -axis motion, a voltage is applied between the inner diameter electrode, Z , and the four outer diameter electrodes, $+X$, $-X$, $+Y$, and $-Y$, with the same voltage applied to all four outer electrodes. This will subject the tube to a field parallel (or antiparallel) to the poling direction. The tube will respond both parallel ($d_{33}E_3$) and transverse ($d_{31}E_3$) to the field. The parallel response will cause an increase or decrease in the tube diameter, but, because of axis-symmetry, this strain will play no role in the STM tip's motion.[†] The transverse response will cause the tube to extend or retract in proportional to the applied field. Using the standard methods of continuum mechanics, the relationship between the change in applied voltage (ΔV) and the change in length (Δz) for an unconstrained tube has been shown to be,¹⁷

$$\Delta z = \frac{d_{31}\Delta V L}{h}, \quad (2.19)$$

with d_{31} , as before; L the tube length; and h the tube wall thickness.[‡] This can be rewritten as,

$$\Delta z = A_z \Delta V, \quad (2.20)$$

where $A_z = d_{31}L/h$. Because of broad manufacturing tolerances (i.e., dimensions plus material properties), A_z is usually determined experimentally. Piezoelectric material

[†]This is also because in most STMs with five-electrode scan tubes, the tip is mounted on a rigid plate attached to the end of the tube. Any radial expansion of the tube will be resisted by the tip mounting. This was not the case with the original five-electrode scan tube where the tip was affixed directly to the inner diameter of the tube.¹⁶

[‡]Eq. 2.19 assumes that $h \ll D$, where D is the tube diameter. This is not actually true for the scan tube used in most STM's. For instance, the scan tube from the STM used for some of the research in this Thesis has dimensions $h = 0.5$ mm and $D = 8$ mm. But violating this assumption is not important since STMs are calibrated before use.

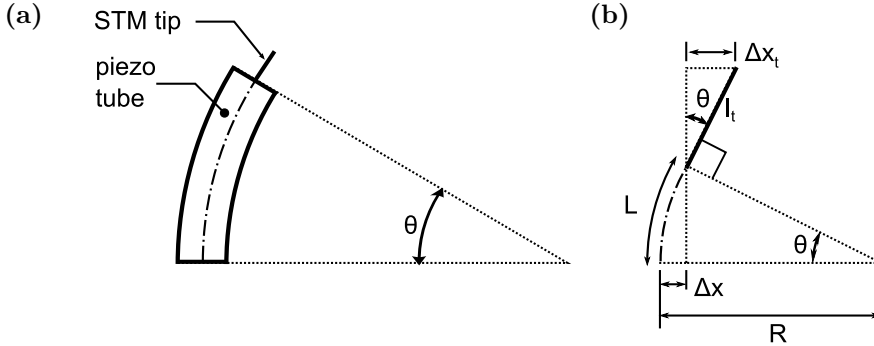


Figure 2.7: (a) Unequal voltages applied to the outer electrodes of the piezoelectric tube will cause it to bend. Because of this the ends of the tube will no longer be parallel and the STM tip will be tilted. (b) Schematic of bent piezoelectric tube showing the contribution to lateral motion from bent tube (ΔX) and tilted tip (ΔX_t).

properties, including d_{31} , are temperature dependent. Typical strain coefficients for the piezoelectric material used in STM scan tubes, type PZT-5A, are $d_{31} = -1.73 \text{ \AA/V}$ at room temperature, and $d_{31} = -0.3 \text{ \AA/V}$ at liquid-helium temperature.¹⁸ Again because of manufacturing tolerances, d_{31} is not known accurately at any temperature, and the STM scan tube should be calibrated as a variety of temperatures. Calibrations are usually made by measuring a known sample. Commonly used reference samples include highly oriented pyrolytic graphite, HOPG,¹⁹ Au(111),²⁰ and even the surface reconstructions of silicon, Si(111)-7x7 and Si(001)-2x1.²¹

Lateral motion is accomplished by applying unequal voltages to the outer electrodes. This will cause it to bend. Analysis of tube bending is more complicated than the analysis of z-axis motion. Consider the case where the inner electrode is grounded, one of the outer electrodes has a voltage applied to it, and the other three outer electrodes are grounded. As the voltage is applied, the quadrant subjected to the field will attempt to respond by lengthening or shortening axially and by expanding or contracting radially, but will be partially constrained by the two quadrants adjacent to it. A full analysis of this can only be accomplished numerically and this has been done with the finite elements method.²² However, by making some reasonable simplifying assumptions, an analytical expression can be found.^{17,23} First consider how a scan tube is typically used in an STM. One end of the tube is rigidly attached to a base while a tip holder is attached to the free end. The effect of the base and tip holder is to constrain the tube ends to remain planar (although not necessarily parallel to each other).[†] Now the force generated by one quadrant will be transmitted to all four quadrants by the base and tip holder and all four quadrants

[†]Without the tip holder, the free end of the piezoelectric tube will not remain planar if unequal voltages are applied to the electrodes. Finite element analysis of a piezoelectric tube with voltage applied to only one quadrant shows that the quadrant subject to voltage will be extended while the adjacent quadrants will be distorted. This can be seen in Fig. 1 of Carr.²²

will be strained. But, as the force is exerted by only one quadrant, the force will not be distributed axis-symmetrically, and a moment will be generated. This moment will cause the tube to bend. Applying a voltage to either the $+X(Y)$ or $-X(Y)$ electrode will bend the tube along the $x(y)$ -axis. Most tube scanners, though, are operated in a symmetric mode. In this mode voltages are applied to pairs of electrodes, either $+X$ and $-X$ or $+Y$ and $-Y$. A voltage is applied to one electrode while a voltage of equal amplitude but opposite polarity is applied to the other electrode. This will double the tube's deflection per volt. In symmetric mode, the lateral tube deflection will be,¹⁷

$$\Delta X \text{ or } \Delta Y = \frac{2\sqrt{2}d_{31}VL^2}{\pi Dh}, \quad (2.21)$$

where V is the voltage applied to one quadrant with $-V$ applied to the opposite quadrant. Note that this only accounts for the deflection of the tube. Because the tube deflects by bending, the free end of the tube—where the tip is mounted—will be tilted (see Fig. 2.7). As it is tilted, the end of the tip will be shifted laterally by more than the end of the scan tube. The tilt angle of the tip can be found from the curvature of bending of the tube. Using the same simplifying assumptions as were used to calculate the tube deflection, the curvature of bending of the tube, R , is given by,

$$R = \frac{\pi Dh}{4\sqrt{2}d_{31}V}. \quad (2.22)$$

From simple geometry, the angle between the top and base of the scan tube, θ , is found to be,

$$\theta = \frac{360L}{2\pi R}. \quad (2.23)$$

Using this angle, the additional lateral deflection of the tip can be found using simple geometry. That is,²³

$$\Delta X_t = l_t \sin(\theta_x), \quad (2.24)$$

$$\Delta Y_t = l_t \sin(\theta_y), \quad (2.25)$$

where l_t is the tip length, and θ_x and θ_y are the bending along the x - and y -axes respectively.

For a typically STM scan tube, R is very large while θ is very small. This can be illustrated with a scan tube from one of the STM's used in this research. The relevant parameters for this tube are $L = 20$ mm, $D = 8$ mm, $h = 0.5$ mm, and $d_{31} = -0.173 \times 10^{-9}$ m/V. With a voltage of 100 V applied symmetrically, the tube deflection will be ΔX or $\Delta Y = 1.56 \times 10^{-6}$ m, with $R = 1.28 \times 10^2$ m and $\theta = 8.92 \times 10^{-2}$ °. Assuming a tip of length $l_t = 6$ mm, the additional lateral deflection due to the tilted tip would be ΔX_t or $\Delta Y_t = 9.35 \times 10^{-7}$ m. That is a

60% increase over the scan tube deflection alone. Although the tip itself is usually shorter than this, the length relevant for this calculation is the distance from the end of the scan tube to the end of the tip, including the thickness of the tip holder, ground plane, etc. Although a calibration can be performed, this calibration should be repeated after every tip change. From Fig. 2.7 it would also appear that tube bending will shift the tip by $\Delta Z_t = l_t(1 - \cos(\theta))$. However, because angle θ is so small, ΔZ_t will be negligible for any practical STM scan tube (for the above example, $\Delta Z_t = 7.3 \times 10^{-9}$ m). A more complete analysis, including the tip being offset from the center of the scan tube has been performed by Yang *et al.*²³

An alternative to the scan tube is to combine two shear piezoelectric actuators and one extension piezoelectric actuator to form an actuator capable of three-axis motion—a three-axis shear/extension actuator. In this scheme, the two shear piezoelectric actuators are mounted with their shear motions oriented orthogonally. Such actuators are sold commercially. They are much more rigid than tube actuators and so have higher first mode frequencies. Finite element calculations show that the first vibration mode for a three-axis shear/extension actuator can easily be an order of magnitude larger than that for scan tube of comparable scan range (≈ 10 kHz versus ≈ 1 kHz). Unfortunately, this rigidity comes at the cost of higher capacitance. For example, one manufacturer offers a three-axis shear/extension actuator with a room-temperature scan range of $10\mu\text{m}$ with a capacitance of 100 nF per axis while their tube scanner of similar scan range has a capacitance of only 10 nF per axis.²⁴ Such large capacitances render shear/extension actuator unsuitable for ultra fast-scanning STM's. As high scan rate is unimportant for STS, one of the STM's used in this research successfully used a shear/extension actuator for scanning.

2.4.3 Coarse Approach

The purpose of the coarse approach mechanism is to bring the tip and sample close enough that electrons can tunnel between them. To make tip and sample changes convenient they should be separated by at least a millimeter. The coarse approach must move this distance in steps smaller than the maximum z-range of the scan tube to avoid crashing the tip into the sample, as has already been explained.

The requirements for an STM coarse approach are quite demanding. As was stated above, the coarse approach should be able to move over distances of millimeters in sub-micrometer steps.²⁵ It must be rigid enough that any compliance is undetectable in either topography or spectroscopy. In general, and especially for variable temperature STM's, the coarse approach should be designed to minimize thermal drift. For use in a high magnetic field, as some of the STM's used in this study were, the coarse approach should also be non-magnetic. Operation in UHV requires that it be resistant to bakeout temperatures of up to 150°C , and also that it functions in UHV.[†] If it is to operate below room temperature it must accommodate thermal expansion and

[†]At room temperature in normal humid air, most surfaces would be expected to be covered in water. This can act as a lubricant. In UHV, some or all of this water will be desorbed. How this effects friction depends upon the surface.^{25,26}

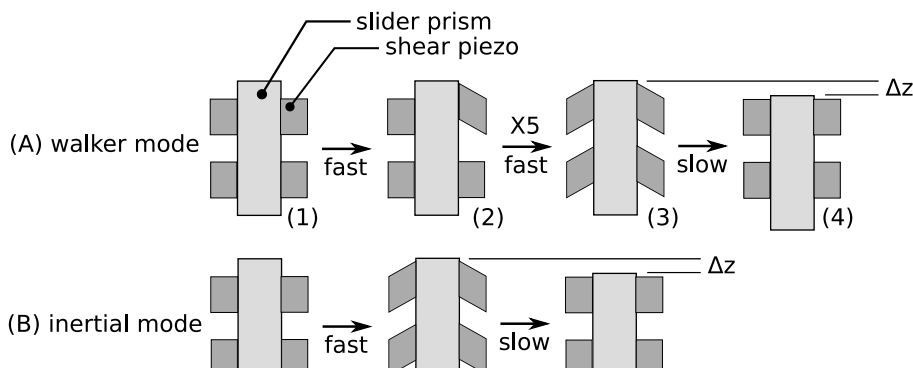


Figure 2.8: Schematic of walker (a) and inertial (b) coarse approach mechanism. Note that the prism is three-sided, so that there are a total of six piezo-actuators.

contraction, and it must not produce more heat than the cooling system can remove. This is particularly true of very low temperature STM's which are usually cooled by very low power systems such as ^3He or dilution refrigerators. Any electrical or mechanical power input must also not act as a conduit for excessive heat flow into the cooler parts of the system.

The solution that best accommodates all of these requirements is a coarse approach using piezoelectric actuators. Since the invention of the STM in 1982,²⁷ many piezoelectrically-driven coarse approach mechanisms have been used successfully. Underlying most of these designs are two types of motion: walker and inertial. The walker mode is similar to animal locomotion, relying on sets of piezoelectric actuators moving out of phase with each other. The inertial mode uses alternating fast and slow piezoelectric actuation and the inertia of a slider mass for motion.

To illustrate the walker and inertial coarse approach modes, the basic operation of the Pan design will be described.²⁸ The design is based on a prism-shaped slider. Further details of this design will be given later. Both modes are illustrated in Fig. 2.8. The Pan design relies on a total of six shear piezoelectric actuators in two rings around the slider. For clarity, only four of them are shown in this Figure. The walker mode functions by moving each actuator individually and in sequence. While the other five remain fixed, one actuator is stepped by applying a rapidly increasing voltage to cause that piezoelectric to shear quickly enough to overcome static friction and slide along the prism [Fig. 2.8(A.2)]. While this actuator is shearing, the prism is held in place by the five stationary actuators. After sliding, the actuator is then held fixed while the other actuators are stepped in turn [Fig. 2.8(A.3)]. Once all six actuators have been sheared, they are then simultaneously retracted slowly back to their starting position [Fig. 2.8(A.4)]. Each cycle will move the prism by the distance the actuators were able to slide along the prism. The prism will only move a small distance with each cycle, typically less than $1\text{ }\mu\text{m}$. Moving a millimeter or more, as

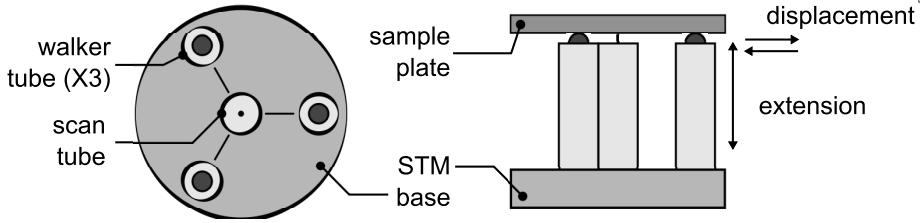


Figure 2.9: Schematic of first incarnation of beetle walker, the Besocke beetle.³⁰ This design provided lateral but no vertical coarse motion.

will be required after a tip or sample change, will require of the order of 1000 cycles.

In the inertial coarse approach mode, all of the actuators are sheared simultaneously. The inertial mode consists of a repeated cycle of alternating fast and slow actuation. During the fast phase, the actuators are sheared quickly enough that the inertial force of the prism will exceed the static friction between the prism and the actuators and the actuators will slide along the prism [Fig. 2.8(B.2)]. Following this, all six actuators are slowly retracted back to their starting position [Fig. 2.8(B.3)]. Because the actuators slid along the prism during the fast phase, there will be a net movement of the prism. The step size will be the distance the actuator slide along the prism, and, as with the walker mode, each step will only move the prism less than $1\mu\text{m}$. Because the actual motion of the actuator and prism is more complicated than described here, the step size will not necessarily be the same as the distance the actuators were sheared.[†]

Survey of Coarse Approach Designs

The original STM coarse approach presented by Binnig *et al* was a horizontal walker.^{16,27} The design, 'the louse', consisted of three feet connected via a piezoelectric body. Walking was performed by clamping two trailing feet, extending the body, clamping the leading foot, releasing the other feet, and contracting the body. Although this system operated successfully, because of issues with thermal drift, it is not the best choice for a variable temperature STM.²⁹ Finally, it is relatively large and cannot be accommodated easily into the bore of a superconducting solenoid.

Another design that appeared in the early days of STM, but, in modified form, is still uses in both homebuilt^{31,32} and commercial³³ STM's is the Besocke beetle design.³⁰ In its first incarnation, it was not capable of vertical coarse motion but, rather, was designed to provide horizontal coarse motion. The design relied upon four 5-electrode piezoelectric tubes, with three tubes used as legs for coarse motion, and one used for scanning (see Fig. 2.9).[‡] The three coarse motion legs form an

[†]For example, in walker mode, the five stationary actuators are compliant and they will deflect somewhat as the walker leg deflects. Similarly, in inertial mode the prism can stop sliding before the actuator stroke is complete, or can continue after the actuators stops.

[‡]Later incarnations have replaced the 5-electrode walker tubes with shear piezoelectric actua-

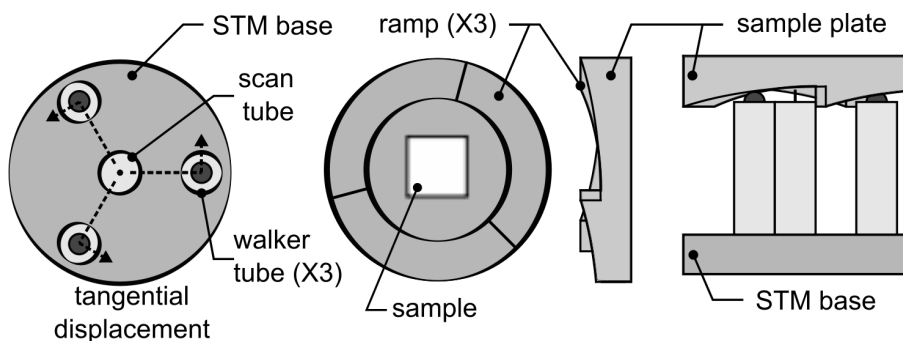


Figure 2.10: Schematic of beetle STM with ramps for coarse approach motion.

equilateral triangle with the scan tube at its center. The sample is mounted onto a flat sample plate which sits on top of the legs. Horizontal motion begins by extending all three legs to separate the tip and sample. All three legs are then rapidly deflected horizontally. If the deflection is rapid enough, then the sample plate's inertia will resist its motion, and the piezoelectric legs will slide under the sample plate. After sliding, the legs are then deflected horizontally back to their starting position slowly enough so as not to slide. The sample plate will now be shifted in relation to the tip by the distance the legs slid. To move further, the cycle can be repeated. To recommence scanning, the walker legs are retracted back until the tip and sample are close enough for tunneling.

The original beetle design can function as a coarse approach if the sample is tilted from horizontal. However a modified version of the beetle was soon conceived by Frohn *et al* that permitted vertical coarse motion with the sample held horizontally.³⁵ The modification involved machining three circular ramps, one for each leg, into the underside of the sample plate (Fig. 2.10). These ramps translate horizontal into vertical motion. The leg deflection must now be tangential to the circle defined by the three coarse motion legs, with the scan tube at its center. The leg deflection will now rotate rather than translate the sample plate. As the sample plate rotates, the legs will walk up or down the ramps, increasing or decreasing the tip-sample separation. The maximum coarse approach motion will be limited because each ramp can only occupy 120° and they cannot be steeper than the legs can climb. The original Frohn design design was limited to a 0.3 mm vertical approach motion.³⁵ The great advantage of the beetle design is that, by making the legs and scan tube from the same piezoelectric material, it is thermally stable and particularly well suited to variable temperature operation.

Soon after the beetle design, a linear inertial STM design was published by Lyding *et al*.²⁹ Like the beetle design, this design was also thermally compensated, but using two concentric piezoelectric tubes, with one for scanning and the other for the coarse

tors.³⁴

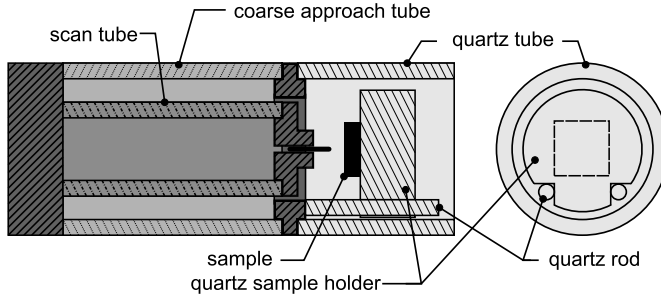


Figure 2.11: Schematic of the STM with linear inertial coarse approach designed by Lyding *et al.*²⁹

approach (see Fig. 2.11). The tip is mounted to the inner piezoelectric tube while a quartz sample holder is clamped to quartz rods connected to the outer tube. Coarse motion is accomplished by applying a sawtooth voltage to the outer piezoelectric tube, making it oscillate in the z direction—fast in one direction, and slow in the other. During this cycle, when the tube is accelerating rapidly, the inertia of the sample holder will cause it to slide along the quartz rods. This design is thermally compensated because both piezoelectric tubes are the same length and because quartz, with its low thermal expansion coefficient, is used for the sample holder and rods. Finally, the thermal expansion of the tungsten tip is compensated for by adding a copper beryllium spacing collar to the outer piezoelectric tube. In this original form, the coarse approach was designed to operate horizontally, requiring the STM to be mounted so as to accommodate this. As with the louse discussed above, this orientation is inconvenient for high magnetic field operation where the diameter of the superconducting solenoid limits the maximum horizontal dimension. Reorienting this design to operate vertically proved to be troublesome. Renner *et al* found that a coarse approach of similar design would not operate vertically with a sawtooth-profile piezoelectric driving voltage.³⁶ They developed a cycloidal voltage profile that would drive their linear inertial motor vertically. In general, the piezoelectric driving voltage profile is critical to the functioning of piezoelectric motors and this will be discussed in more detail below. A later incarnation of the linear inertial motor was capable of x , y , z motion.³⁷ This design combined a slider mounted on three orthogonal rails with a five-electrode piezoelectric tube capable of 3-axis driving motion.

The final STM design to be discussed here features a coarse approach capable of both inertial and walker motion and is, in modified form, the coarse approach mechanism chosen for the homebuilt STM's used in this research. The design, invented by Pan *et al.*,²⁸ consists of a triangular cross-section prism (with truncated vertices) and three pairs of shear piezoelectric actuators, one pair in contact with each face (see Fig. 2.12). Two pairs of these actuators are attached to a rigid STM body. The remaining pair is attached to a plate and pressed against the prism with a spring. The normal force between the actuators and the prism is varied by adjusting the spring

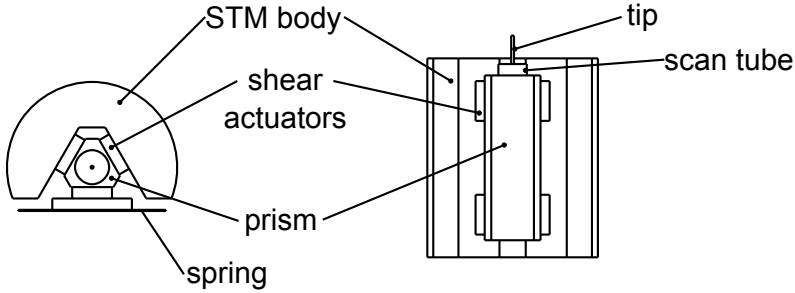


Figure 2.12: Schematic of the Pan-design STM coarse approach.²⁸

force. In the original publication this coarse approach was operated in only the walker mode. The advantages of this design when used in the walker mode include reliability and suitability for vertical operation.²⁸ Because the walker mode does not rely on inertia, the step size when walking against gravity or with gravity is about the same. Nevertheless, this design can also be used in inertial mode, which is how this design was used in this research. To operate in walker mode, six pairs of wires are needed, one pair for each piezoelectric actuator. In inertial mode, only one pair of wires is required as all six piezoelectric actuators are driven simultaneously.

Coarse Approach Motors at Low Temperatures

Low temperature poses severe challenge to STM coarse approach motors. This challenge stems primarily from weakened piezoelectric actuators, but can be exacerbated by increased friction caused by frozen contaminants. Piezoelectric actuators are weaker at low temperatures because the piezoelectric coefficient is reduced. For example, at liquid helium temperature (4.2 K), the piezoelectric coefficient, d_{31} , of PZT-5A is reduced to about $\approx 17\%$ of its room temperature (293 K) value (from $-1.73 \text{ \AA/V}$ to $-0.30 \text{ \AA/V}$).¹⁸ This means that at 4.2 K, for a given applied voltage, a piezoelectric actuator will only be able to move by $\approx 17\%$ of the distance it would move at room temperature but also be only able to exert a force $\approx 17\%$ of what it could at room temperature (see Eq. 2.15).

This reduced force can be a significant issue for both inertial and walker modes where the piezoelectric actuators must be able to overcome static friction. During the sliding portion of the cycle, the shear piezoelectric actuators of a Pan-design STM need to exert a force in excess of the static friction between them and the prism. For Coulomb friction between two surfaces not in relative motion, the (static) friction force is $F_f \leq \mu_s F_N$, where μ_s is the coefficient of static friction, and F_N is the normal force between the surfaces. This static friction will inhibit the surfaces sliding against each other until the force applied tangential to the surface, F , exceeds the maximum static friction, $F_f^{max} = \mu_s F_N$. Once the surfaces begin to slide, the friction force will be reduced to $F_f = \mu_k F_N$, where μ_k is the coefficient of kinetic friction, and where

$\mu_k < \mu_s$. Sliding will continue until $F < \mu_k F_N$. Because experiments have shown that for some material combinations in contact under high vacuum, including sapphire against sapphire, μ_s does not change significantly between room temperature and 4.2K,²⁶ and the piezos will still need to overcome the same static and kinetic friction as at room temperature. Further compounding this, at low temperatures, contaminants can freeze onto the sliding surfaces and, possibly, dramatically increase μ_s and μ_k . A combination of weakened piezoelectric actuators and frozen surface contaminants can severely reduce the reliability of low-temperature STM coarse approaches.

Two of the STM's used in this research were required to function at low temperatures. While one of these STMs was used exclusively in UHV, the other was operated in flowing helium boil-off gas. Despite similar coarse approach designs, the UHV STM was more reliable at low temperatures ($T < 40$ K) than the He-gas STM. The most likely explanation is that there were more frozen contaminants on the sliding surfaces of the He-gas STM than on the sliding surfaces of the UHV STM. This is simply because the UHV STM is baked out before it is cooled and the He-gas STM is not. Although helium boil-off gas is likely free of a significant concentration of contaminants, neither the He-gas STM nor the variable temperature insert (VTI) in which it was operated were as free of contaminants, especially water, as the UHV STM and UHV chamber. Instead of a bake-out—which was not possible, the He-gas STM was inserted into the VTI and warmed to ≈ 350 K for up to several hours while enveloped in flowing helium boil-off gas. The combination of dry helium boil-off gas and warming will remove some of the adsorbed water on the STM sliding surfaces, but not as much as would be removed by a UHV bake-out.[†]

Beyond their different operating conditions, the most significant difference between the UHV STM and the He-gas STM was in the materials used for their sliding surfaces. While the UHV STM used a titanium carbide-coated prism in contact with alumina, the gas-flow STM used a sapphire prism in contact with sapphire. However, this difference is unlikely to be the cause of the He-gas STM's poor low-temperature performance. A third STM was built with the same sliding surfaces as the UHV STM. This STM performed especially poorly in He-gas.[‡] This leaves surface contamination, probably water, combined with piezoelectric actuators weakened at low-temperature as the most likely causes of poor low-temperature performance of the gas-flow STM coarse approach. A UHV bake-out will remove some of the contaminants and most likely increase the reliability of a low-temperature Pan-style STM.

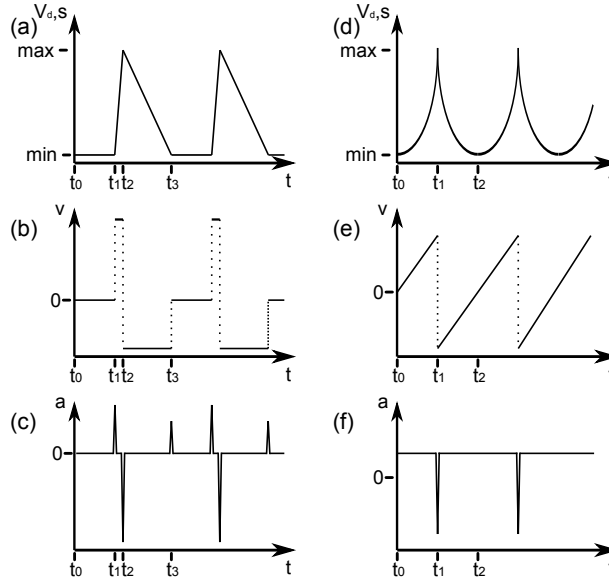


Figure 2.13: Illustration of the saw-tooth [(a),(b), and (c)] and cycloidal [(d),(e), and (f)] voltage profiles (V_d), and corresponding actuator position (s), velocity (v), and acceleration (a).

Coarse Approach Driving-Voltage Profile

The voltage profile used to drive a piezoelectric actuator in an STM coarse approach is critical to its function at low temperature, and particularly when operating vertically against gravity. The first inertial STM coarse approach, the Lyding STM discussed above, was driven by a saw-tooth profile [Fig. 2.13(a)], but could only function horizontally.²⁹ This design was then adapted for vertical operation by Renner *et al* by, amongst other things, changing the voltage profile used.³⁶ This modification was deemed necessary because a saw-tooth profile has three sharp turning points that will cause high acceleration and thus—possibly—sliding motion in both directions. This is a rather subtle point and will be discussed in more detail in what follows.

An illustration of a saw-tooth profile of the driving voltage (V_d) and the corresponding actuator position (s), velocity (v) and acceleration (a) are shown in Fig. 2.13(a), (b), and (c). The V_d cycle consists of three phases: a quiescent phase be-

[†]Baking out involves pumping the system down to about 10^{-8} mBar, then heating the chamber to above 100°C for several days while pumping continuously. Water is the main contaminant removed during bake-out. Adsorbed water will be desorbed very quickly from the surface, while absorbed water must first diffuse to the surface. As diffusion is thermally activated, UHV chambers are heated to expedite the process.

[‡]During preliminary tests in the boil-off gas within the neck of a helium Dewar, the coarse approach of this STM failed to function even while still above 200 K .

tween t_0 and t_1 ; a fast ramp phase between t_1 and t_2 ; and a slow ramp phase between t_2 and t_3 . During the quiescent phase the actuator does not move. At t_1 the fast ramp begins and V_d is ramped up to the maximum voltage as fast as the driving electronics will permit. At t_2 , the slow ramp begins and V_d is decreased at a rate lower than during the fast ramp. During both the fast-ramp and the slow ramp the actuator will be moving at an approximately constant speed.[†] At t_1 , t_2 , and t_3 the actuator must apply a brief force or impulse to the slider mass to change the its velocity. This is illustrated in Fig. 2.13(c). During these three impulses the actuator will be accelerating and thus applying a force to the slider. Between impulses the slider will be moving at an approximately constant velocity and the actuator will not be applying a force to it. Only when the actuator is applying a force can the slider begin to slide.[‡] Thus sliding can commence during any or all of the three impulses of each cycle. Two of these impulses apply a force in one direction while the third applies a force in the opposite direction. The slider can therefore slide in both directions during each cycle. Ideally the velocity profile is tuned such that only during the larges impulse, the one at t_2 , will the actuator apply force sufficient to overcome static friction and cause sliding.

Other voltage profiles have been proposed to sidestep the careful tuning required for the saw-tooth profile. After failing to operate an inertial coarse approach oriented vertically with a saw-tooth voltage profile, Renner *et al* developed a quadratic, cycloidal voltage profile to drive their piezoelectric actuators [Fig. 2.13(d)]. They hypothesized that during each saw-tooth cycle the coarse approach moves forward at t_2 but backwards at t_1 . When combined with gravity—as would be the case with the course approach mounted vertically, the course approach ceases to function. In contrast, the quadratic profile has, except at the cusps, a constant, low acceleration. At the cusps, the actuator velocity is reversed by an impulse [Fig. 2.13(f)]. The cycloidal voltage profile must be tuned such that during the constant acceleration phase the actuator force is less than F_f^{max} , while during the impulse the actuator force exceeds it. Because there is only one impulse in each cycle, there will only be sliding in one direction, and therefore the coarse approach should move more efficiently.

Reversing the coarse approach direction can be accomplished in variety of ways. For the saw-tooth profile, reversing the profile in time or polarity will work. For the cycloidal profile, the polarity must be reversed.

Mariotto *et al* studied a Pan-style coarse approach in both inertial and walker modes, mounted vertically, but only at room temperature.²⁵ They applied a voltage profile consisting of a voltage step followed by a quarter sine-wave decrease to zero voltage (see Fig. 2.14). They found that the in the walker mode the step size per cycle was greater than in the inertial mode. They also found that the actual slope of the voltage step, limited by the high voltage amplifier slew rate and the capacitance being

[†]At driving frequencies less than the natural frequency of the piezoelectric actuator-coarse approach system, the actuator position will follow the driving voltage reasonably closely and, therefore, $s \propto V_d$.

[‡]The force must also exceed the maximum static friction, F_f^{max} , between the actuator and the slider for sliding to occur.

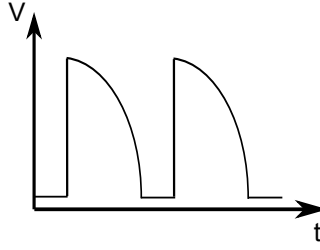


Figure 2.14: Quarter sine voltage profile used by Mariotto *et al.*²⁵

driven, determined the step size in both inertial and walker modes. That the voltage slope is critical is not entirely obvious because for any sliding to occur, whether in the inertial or walker mode, the piezoelectric must accelerate and a linear voltage increase has zero acceleration. The authors attribute the slope dependence to the viscoelastic properties of the epoxy used in assembling the shear piezoelectrics.

For the STMs used in this study, when at room temperature, even if mounted vertically, the particular voltage profile used was not critical, and a variety of amplitudes and frequencies could be used to drive the coarse approach. Once cooled below room temperature, though, the voltage profile, amplitude, and frequency become critical. Even small changes to the driving frequency or amplitude can result in the coarse approach not functioning. This indicates that the simple picture of a piezoelectrically driven coarse approach described above is incomplete.

2.5 Measuring the Tunneling Current

The tunneling current needs to be measured for both feedback control and for tunneling spectroscopy. Typically, a transimpedance amplifier is used. This type of amplifier outputs a voltage that is proportional to the input current.

2.5.1 Amplifier Basics

The basic transimpedance amplifier circuit is conceptually remarkably simple and involves only one resistor and one operational amplifier (op-amp) [Fig. 2.15(a)].

Assuming an ideal op-amp and ignoring the feedback resistor parasitic capacitance (C_{fb}) the output voltage from the circuit shown in Fig. 2.15(a) will be,

$$V_o = -I_i R_{fb}, \quad (2.26)$$

where V_o is the output voltage, I_i is the input current, and R_{fb} is the feedback resistor. Although this circuit works, in order to measure the very small tunneling currents usually encountered in STM, the feedback resistor needs to be very large. The tunneling resistance in an STM typically ranges from about 100 M Ω to 10 G Ω , while the bias voltage ranges from about 100 mV to 1 V. This will mean that a typical

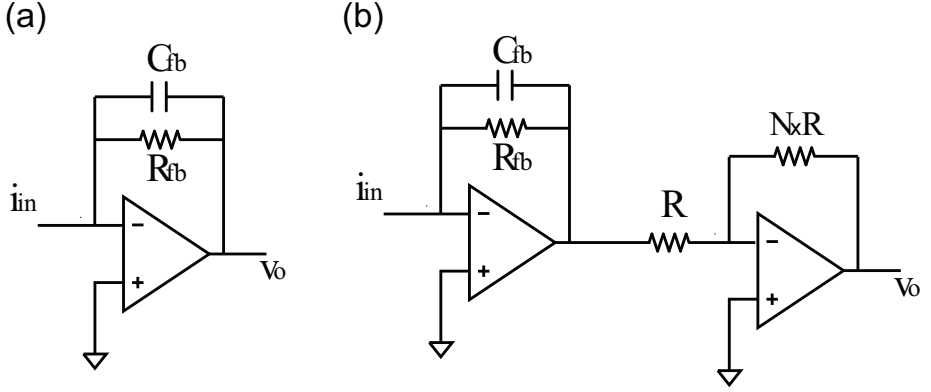


Figure 2.15: Schematic of (a) transimpedance amplifier and (b) transimpedance amplifier with second stage of gain N . Adapted from Refs. 10,33,38.

tunneling current will range from about 10 nA to 100 pA. To produce a convenient output voltage, $V_o = 1$ V, the amplifier gain needs to be between 10^8 and 10^{10} V/A, requiring a feedback resistor of between 100 M Ω and 10 G Ω .

Using such large resistances offer both advantages and a disadvantages. On the plus side, the thermal current noise from the feedback resistor, the major source of noise in transimpedance amplifiers,¹⁰ decreases as the resistance increases. The thermal current noise (or Johnson noise), I_n , is given by,^{10,38}

$$I_n = \sqrt{\frac{4k_B T B}{R_{fb}}}, \quad (2.27)$$

where k_B is the Boltzmann constant, T is the resistor temperature, and B is the bandwidth over which the noise is measured. It can be seen that, for a given bandwidth, increasing the resistance will decrease the current noise. This suggest that R_{fb} should be maximized to minimize noise. Unfortunately, as we will now see, because of parasitic capacitance, increasing R_{fb} will also reduce the amplifier bandwidth.

All real resistors suffer from parasitic capacitance, C_{fb} . This capacitance is equivalent to a capacitance in parallel with the feedback resistor [Fig. 2.15(b)]. At higher frequencies, C_{fb} will short out R_{fb} , reducing the effective feedback resistance, and, as can be deduced from Eq. 2.26, reduce the gain of the amplifier. Although parasitic capacitances are typically small, on the order of 1 pF,¹⁰ when combined with very large resistances, the effect becomes significant. Including C_{fb} in parallel with R_{fb} the gain, G , becomes,

$$G = \frac{V_o}{I_i} = \frac{R_{fb}}{\sqrt{1 + (2\pi C_{fb} R_{fb})^2}}, \quad (2.28)$$

The addition of the parasitic capacitance has made the amplifier into a low-pass filter with a -3 dB point at frequency,¹⁰

$$f = \frac{1}{2\pi R_{fb} C_{fb}}. \quad (2.29)$$

Substituting typical values for an STM transimpedance amplifier, $R_{fb} = 100 \text{ M}\Omega$ and $C_{fb} = 1 \text{ pF}$, results in a bandwidth of $f \approx 1.5 \text{ kHz}$, which is quite limiting in practical use.

A narrow transimpedance amplifier bandwidth imposes severe restrictions on both topographic and spectroscopic measurements. These include requiring more time to measure topography and spectroscopy and, possibly, making modulation techniques infeasible.

Topographic measurements will take longer because the feedback mechanism uses the tunneling current for error correction. To avoid losing fine detail from topography and to avoid crashing the tip into the sample the scanning speed must be reduced.

Spectroscopic measurements will also take longer. To compensate for a narrow bandwidth, the bias voltage sweep-rate must be reduced, increasing the IV curve measurement time. This can be a significant problem for dense spectroscopy maps requiring hundreds of IV measurements, particularly if averaging is necessary and multiple measurements must be made at each point. Increased measurement time also exacerbated problems associated with drift. During a fixed-gap IV curve measurement the bias voltage is swept with the feedback disengaged.[†] During this time the tip-sample distance can change because of thermal drift. Because of the exponential dependence of tunneling current on tip-sample distance, a small change in tip-sample distance can cause a large change in tunneling current, large enough to distort or obscure the spectroscopic information contained in the measurement.

Lastly, if modulation techniques are used, a narrow amplifier bandwidth will require that either the modulation frequency be decreased to within the bandwidth or that the modulation amplitude be increased to compensate for the reduced gain at the modulation frequency. Neither option is desirable. The ideal modulation frequency is above the feedback bandwidth but within the transimpedance amplifier's bandwidth. If the modulation frequency is within the feedback bandwidth, then the tip height will also be modulated. If the modulation frequency is above the feedback bandwidth and if the modulation amplitude is increased to compensate for this, then the spectroscopic data will be broadened, and fine detail being lost. For modulation amplitudes of more than a few percent of the bias voltage, the measurement will no longer be a measure of the IV curve slope.

2.5.2 Practical Transimpedance Amplifier Design

Because of the limitations imposed by the narrow bandwidth, practical STM transimpedance amplifiers are usually a modified version of the simple, one large resistor

[†]If it were not disengaged the feedback would adjust the tip-sample distance to compensate for changes in bias.

amplifier. Three variants of the one-resistor transimpedance amplifier will be discussed here: a two-stage amplifier, a T-network feedback amplifier, and a compensating second-stage amplifier.

Two-Stage Amplifier

The two-stage amplifier consists of a transimpedance amplifier followed by a voltage amplifier. A simplified circuit diagram of this scheme is shown in Fig. 2.15(b). Because the voltage amplifier will boost the overall amplifier gain, the transimpedance amplifier gain can be reduced by using a smaller feedback resistor. This smaller feedback resistor will reduce the impact of parasitic capacitance and increase the amplifier bandwidth (see Eq. 2.29). The overall gain can be made as large as the overall gain of a single-stage transimpedance amplifier with a larger feedback resistor. The two-stage cascade amplifier is the solution favored by RHK, the manufacturer of some of the commercial amplifiers used in this study.³³ These amplifiers combine a transimpedance amplifier with a $1\text{ M}\Omega^\dagger$ feedback resistor followed by a 100X gain voltage amplifier. This is an overall gain of 10^8 V/A . The disadvantage of this scheme is that the resistor thermal noise of the first stage will increase because of the smaller feedback resistor and the second stage will amplify this extra noise. To address this issue, one variant of this amplifier features a second stage with a variable bandwidth, low-pass filter. This allows the bandwidth to be trimmed to the minimum required for scanning and spectroscopy, cutting off higher frequencies that contribute only to the noise floor.

T-Network Feedback Amplifier

A second way to expand the transimpedance amplifier bandwidth is to replace the single large feedback resistor with an impedance T-network [see Fig. 2.16(a)]. This T-network consists of three impedances, one of which is connected to ground, with each impedance composed of either a resistor, a capacitor, or a resistor in parallel with a capacitor. Two variants of this will be discussed here: a resistor network replacing a single large feedback resistor,¹⁰ or directly compensating for the parasitic capacitance in the feedback of the transimpedance amplifier itself with a resistor-capacitor (R-C) combination.^{10,39,40} Circuit schematics of the resistor network and R-C compensating feedback are shown in Fig. 2.16(b) and (c). Both of these techniques can be understood as special cases of a more general impedance network feedback.

Fig. 2.16(a) shows a simplified circuit diagram of a transimpedance amplifier with a T-network feedback of three impedances, Z_1 , Z_2 , and Z_3 , each of which can represent a resistor, a capacitor, or a parallel resistor and capacitor. Its transfer function is defined as the ratio of the output voltage to the input current, $G = v_o/I_{in}$. To find this, first sum the currents at the common connection point of the three

[†]We modified this amplifier to increase the gain by substituting a $10\text{ M}\Omega$ or $100\text{ M}\Omega$ feedback resistor to boost the overall gain to 10^9 V/A and 10^{10} V/A respectively.

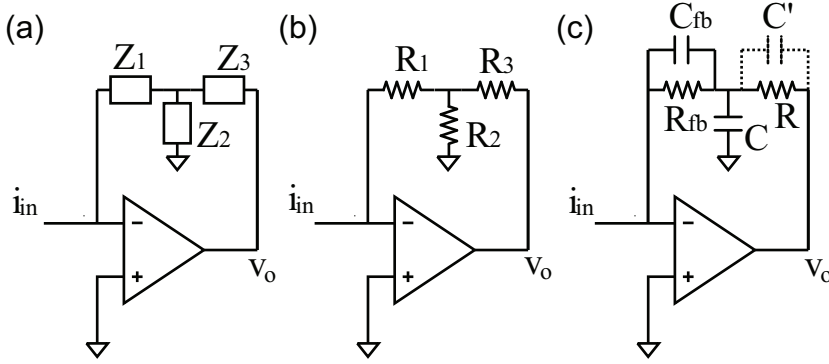


Figure 2.16: Schematic of transimpedance amplifier with (a) impedance network feedback, (b) resistor network feedback, and (c) feedback compensation. Schematics (b) and (c) are special cases of (a). Adapted from Refs. 10,38–40.

impedances,³⁸

$$\frac{(0 - V_1)}{Z_1} + \frac{(0 - V_1)}{Z_2} + \frac{(V_o - V_1)}{Z_3} = 0. \quad (2.30)$$

If the op-amp is assumed to be ideal, no current will flow into the $V_{(-)}$ input, and all of the input current must flow through the feedback. For an input current of I_i , therefore, the voltage drop across Z_1 will be,

$$(0 - V_1) = I_i Z_1. \quad (2.31)$$

This can then be combined with Eq. 2.30 to solve for the amplifier gain,

$$G = \frac{V_o}{I_i} = - \left[1 + \frac{Z_3}{Z_1} + \frac{Z_3}{Z_2} \right] Z_1. \quad (2.32)$$

The gain of the two special cases is calculated by substituting specific values for the three impedances.

The resistor network consists of three resistors connected in a T-network. As will be discussed below, the resistance of each of the three resistors can be smaller than that needed for a single-feedback resistor amplifier, and, because of this, the parasitic capacitance will not reduce the bandwidth as significantly. For a resistor network with $Z_1 = R_1$, $Z_2 = R_2$, and $Z_3 = R_3$,[†] Eq. 2.32 gives,

$$\frac{V_o}{I_i} = - \left[1 + \frac{R_3}{R_1} + \frac{R_3}{R_2} \right] R_1 = - \left[R_3 + R_1 \left(1 + \frac{R_3}{R_2} \right) \right]. \quad (2.33)$$

[†]In this analysis, impedance Z_1 is taken as a purely resistive, without a parallel parasitic capacitance. This is because for smaller resistances, the -3 dB point frequency, which is inversely proportional to the product of resistance and capacitance (Eq. 2.29), should be beyond the bandwidth of interest. To analyze the resistor with parallel capacitance, the impedance of a resistor in parallel with a capacitor can be substituted for Z_1 .

This equation shows how the resistor network boosts the gain. In addition to a small gain from R_3 directly, the voltage divider formed by R_2 and R_3 acts to multiply the gain of R_1 . This is because the op-amp must increase v_o to compensate for the voltage divider which reduces the voltage that R_1 is subject to (V_1). The resistance of R_1 can be chosen so that it and its parasitic capacitance will lead to the desired bandwidth. Then R_2 and R_3 can be chosen so that their ratio, R_3/R_2 , provides the necessary boost to the gain. As with the cascade amplifier discussed above, the drawback of this design is that, because the feedback resistors are smaller, the thermal noise current noise will be larger.

The R-C compensating feedback consists of a feedback resistor, R_{fb} , with parasitic capacitance in parallel, C_{fb} , and a second resistor, R , and capacitor, C , that act to compensate for this parasitic capacitance. The third capacitance, C' , shown in Fig. 2.16(c) is optional and its significance will be discussed below. For the R-C feedback compensation, R_{fb} is sized to provide all of the gain needed while the R-C portion of the feedback is sized to compensate for the parasitic capacitance and expand the bandwidth. Again, Eq. 2.32 can be used to analyze this circuit. Impedance Z_1 will now be resistor, R_{fb} , in parallel with a capacitor, C_{fb} . Thus,

$$Z_1 = \frac{R_{fb}}{1 + i\omega R_{fb}C_{fb}}. \quad (2.34)$$

Now set $Z_2 = 1/i\omega C$ and $Z_3 = R$ and substitute into Eq. 2.32

$$G = \frac{V_o}{I_i} = - \left[R + R_{fb} \frac{(1 + i\omega RC)}{(1 + i\omega R_{fb}C_{fb})} \right] \quad (2.35)$$

If $RC = R_{fb}C_{fb}$ then C_{fb} will be perfectly compensated for by R and C , and the amplifier frequency response will be flat.^{10,40} A second capacitor can be added in parallel to R to reduce the bandwidth to the minimum needed and thereby limit the amplified noise.⁴⁰ A disadvantage of this design is that it is unstable for high input capacitance.⁴¹ As long coaxial cables are unavoidable for the low-temperature, high magnetic field STMs used in this research, R-C feedback compensation would be impractical.

Compensating Second Stage

A third method to compensate for the bandwidth-limiting parasitic capacitance is to follow the transimpedance amplifier with a high-frequency boosting second stage.^{41,42} A simplified circuit diagram of the design proposed by Carla *et al* is shown in Fig. 2.17.⁴² In this scheme, the first stage consists of a transimpedance amplifier with a single feedback resistor large enough to provide sufficient gain and to achieve low thermal current noise. As has already been discussed, a large resistor in parallel with its parasitic capacitance will reduce the bandwidth of the amplifier. Including parasitic capacitance, the transfer function of the first stage is,

$$H_1(\omega) = \frac{R_{fb}}{1 + i\omega R_{fb}C_{fb}}. \quad (2.36)$$

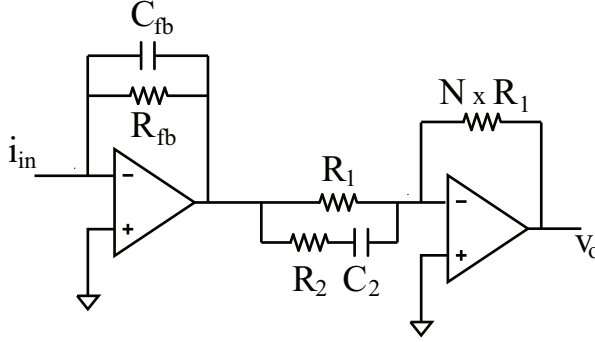


Figure 2.17: Schematic of transimpedance amplifier with high-frequency boosting second stage. Adapted from Ref. 42

This is a low-pass filter with bandwidth $\omega_{h1} = 1/R_{fb}C_{fb}$. To expand the bandwidth, the second stage must invert this and flatten out the frequency response. The second stage proposed by Carla et al is just a voltage amplifier with a resistor, R_2 , and capacitor, C_2 , in parallel to R_1 . The parallel resistor-capacitor will act to short out R_1 , increasing the second-state gain at higher frequencies. The transfer function of the second stage is,

$$H_2(\omega) = N \frac{1 + i\omega C_2(R_1 + R_2)}{1 + i\omega R_2 C_2}. \quad (2.37)$$

where N is the second stage low-frequency gain. If $C_2(R_1 + R_2)$ is set equal to $R_{fb}C_{fb}$, then the transfer function of the combined two-stage amplifier will be,

$$H(\omega) = N \frac{R_{fb}}{1 + i\omega R_2 C_2}. \quad (2.38)$$

The overall amplifier bandwidth is $\omega_h = 1/R_2 C_2$ while the overall low-frequency gain is NR_{fb} . The second stage has perfectly compensated for the parasitic capacitance of the first-stage feedback resistor, but still has a limited bandwidth. Nevertheless, because it is the sum of R_1 and R_2 multiplied by C_2 that is used to compensate for the parasitic capacitance, there remains some flexibility in choosing R_2 and C_2 , allowing some control over the bandwidth, ω_h . R_{fb} can now be set so as to minimize the thermal noise current. Other researchers have proposed similar high-frequency boosting stages.^{41,43}

2.5.3 Amplifier Noise

The feedback resistor Johnson noise is only one of a number of amplifier noise sources. The op-amp itself contributes noise and is exacerbated by the particular way that transimpedance amplifiers are used in STM current measurements. There exists a rich

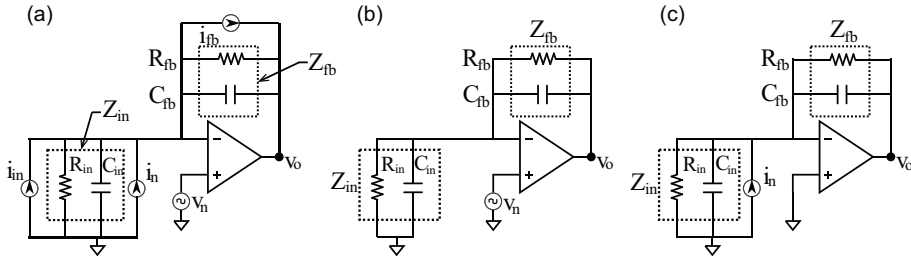


Figure 2.18: Noise model of STM transimpedance amplifier. (a) Noise model showing all noise sources. (b) Noise model showing only the op-amp voltage noise (v_n). (c) Noise model with noise current (i_{eq}) equivalent to v_n . Adapted from Refs. 38,42,44,45.

literature of analyzing noise in transimpedance amplifiers. Much of this analysis concerns photodiode applications, but it can easily be adapted to STM transimpedance amplifiers.

With noise sources included, a STM transimpedance amplifier can be modeled as shown in Fig. 2.18(a).^{38,42,44,45} These noise sources are the Johnson noise of the feedback resistor (i_{fb}), the op-amp current noise (i_n), and op-amp voltage noise (v_n). The resistor current noise is produced by the random thermal motion of current carriers and was discussed above (Eq. 2.27). This noise is modeled as a current source in parallel with a noiseless resistor. Johnson noise is the minimum noise possible noise for a resistor of a given value. Real resistors are noisier, though metal resistors come close to the minimum thermal noise.¹⁰ The op-amp noises, v_n and i_n , are generated by the op-amp itself and are usually specified in data sheets issued by the manufacturer; v_n is specified as a voltage at positive input of the op-amp, $v_{(+)}$, while the current noise is specified as a current in parallel with the input current.

Also shown in Fig. 2.18(a) are an input resistance (R_{in}) and an input capacitance (C_{in}). This input impedance (Z_{in}) is the sum of the capacitance across the input terminals of the op-amp, the capacitance between the tip and sample, and the capacitance of the coaxial cable connecting the STM to the amplifier. The input capacitance of op-amps used for STM current measurements is typically about 3 pF,[†] and while the tip-sample capacitance is negligible,⁴⁶ the coaxial cables connecting the tip/sample to the transimpedance amplifier have capacitances of ~ 100 pF per meter. The amplifier input coaxial cable need not be very long for the capacitance of the cable to dominate the other sources of capacitance. As will be shown, large input capacitances lead to substantial noise. Finally, the feedback impedance (Z_{fb}) consisting of R_{fb} and C_{fb} in parallel, will be included in the model.

To understand the relative importance of the noise sources, the equivalent input current spectral density of each of the noise sources should be calculated. In accord

[†]Three op-amps commonly used for STM transimpedance amplifiers are the OPA111⁴¹ and OPA656 from Texas Instruments and the AD549⁴² from Analog Devices. All have input capacitances of less than 3 pF.

with the principle of superposition, each noise can be treated separately, then summed quadratically. When modeling each noise, the op-amp itself will be treated as noiseless. In all of the following analysis, the virtual short-circuit approximation will be assumed. This will mean that the positive and negative inputs of the op-amp will be at the same potential, and that no current can flow into or out of either of them.

First consider the op-amp noise voltage, v_n . The amplifier with all other noise sources removed and no input current is illustrated in Fig. 2.18(b). Because this noise is assumed to be connected at the positive input of the op-amp, $v_{(+)} = v_n$. This would cause $v_{(-)} \neq v_{(+)}$ and the op-amp will respond by driving v_o . With $v_o \neq 0$, a current will flow from the output of the op-amp and through Z_{fb} . Because no current can flow into the negative input of the op-amp, all of the current will then flow through Z_{in} and the current will be,

$$I = -v_o \frac{1}{(Z_{in} + Z_{fb})} \quad (2.39)$$

The voltage drop across the input impedance will be,

$$0 - v_{(-)} = IZ_{in} \quad (2.40)$$

Eliminating I from Eq. 2.39 with Eq. 2.40, and solving for v_o gives,

$$v_o = -v_{(-)} \frac{(Z_{in} + Z_{fb})}{Z_{in}} \quad (2.41)$$

Since the op-amp is assumed to be ideal, v_o will be driven until $v_{(-)} + v_{(+)} = 0$. This and Eq. 2.41 can be used to solve for the output voltage resulting from a noise voltage at the op-amp's positive input terminal,

$$v_o = -v_n \frac{(Z_{in} + Z_{fb})}{Z_{in}} \quad (2.42)$$

In order to compare it to other noise sources, v_o must be converted to an equivalent input noise current at the op-amp input. Illustrated in Fig. 2.18(c) is the equivalent circuit with v_n removed and replaced by an equivalent current, i_{eq} . By the virtual-short approximation, $v_{(-)} = v_{(+)} = 0$ V, and there is no voltage drop across Z_{in} , and no current can flow through it. All of the current, therefore, will flow through Z_{fb} ,

$$v_o = i_{eq}Z_{fb} \quad (2.43)$$

This can be combined with Eq. 2.42 to eliminate v_o and solve for i_{eq} ,

$$i_{eq} = -v_n \left(\frac{Z_{in} + Z_{fb}}{Z_{in}Z_{fb}} \right) = -v_n \left(\frac{1}{Z_{in}} + \frac{1}{Z_{fb}} \right) \quad (2.44)$$

With this, the equivalent input spectral density current can be calculated for the three noise sources considered in this analysis,

$$i^2 = i_n^2 + v_n^2 \left(\frac{1}{Z_{in}} + \frac{1}{Z_{fb}} \right)^2 + \frac{4k_B T B}{R_{fb}} \quad (2.45)$$

Now the relative noise contribution from each sources can be compared. The current noise (i_n) intrinsic to the op-amp is fixed for each op-amp and a matter of choosing an op-amp with lower input current noise. Reducing the noise current caused by v_n can be accomplished by either minimizing v_n itself or maximizing Z_{in} and Z_{fb} .⁴² Once again, v_n is fixed for each op-amp, and can only changed by selecting another op-amp. Both Z_{in} and Z_{fb} are combinations of resistors and capacitors in parallel. The impedance for a resistor (R) in parallel with a capacitor (C) is,

$$Z(\omega) = \frac{1}{1/R + i\omega C}. \quad (2.46)$$

Thus, to increase the impedance, increase R and decrease C . Substituting Eq. 2.46 into Eq. 2.45 gives,

$$i^2 = i_n^2 + v_n^2 (1/R_{in} + i\omega C_{in} + 1/R_{fb} + i\omega C_{fb})^2 + \frac{4k_B T B}{R_{fb}} \quad (2.47)$$

The input resistance is a combination of circuit board isolation, wiring insulation, and tip or sample isolation. With proper design, $R_{in} \gg R_{fb}$, and R_{in} can be neglected. The feedback impedance, C_{fb} , cannot be reduced below the intrinsic parasitic capacitance of the feedback resistor,[†] but, if almost any length of coaxial cable connects the STM to the transimpedance amplifier input, then $C_{in} \gg C_{fb}$, and C_{fb} can be neglected. Eq. 2.47 reduces to,

$$i^2 = i_n^2 + v_n^2 (i\omega C_{in} + 1/R_{fb})^2 + \frac{4k_B T B}{R_{fb}} \quad (2.48)$$

To decrease the output noise current, decrease C_{in} and increase R_{fb} .

The final noise source is the Johnson noise of the feedback resistor. As can be seen from Eq. 2.45, increasing R_{fb} will directly reduce the feedback resistor noise. In addition, because of the parasitic capacitance, increasing the feedback resistance will narrow the amplifier bandwidth, and this will also decrease the amplifier noise.

Now a note concerning the current noise spectral density versus the voltage noise spectral density of the feedback resistor Johnson noise. Rewriting the current noise spectral density in terms of voltage,

$$v_{thermal} = i_n R_{fb} = \sqrt{\frac{4k_B T B}{R_{fb}}} R_{fb} = \sqrt{4k_B T R_{fb} B}, \quad (2.49)$$

It seems that, in contrast to the current noise spectral density (Eq. 2.27), the thermal voltage noise will be larger for larger resistors. Thus, because $v_o = v_{thermal}$, the noise voltage at the output will also increase with increasing R_{fb} . This is true, but it is not the absolute size of the output noise that is important, but rather the signal to

[†]Large resistors with very low parasitic capacitance are available. Ciofi *et al* report of commercially available 1 G Ω -plus resistors with parasitic capacitances of ~ 100 fF.⁴³

noise ratio (SNR). The amplifier output voltage (v_s) for an input signal current (I_s) is given by,

$$v_s = R_{fb} I_s. \quad (2.50)$$

Thus the signal will increase as $v_s \sim R_{fb}$ whereas, from Eq. 2.49, the Johnson noise will increase as $v_n \sim \sqrt{R_{fb}}$. The SNR will therefore increase as $\text{SNR} \sim \sqrt{R_{fb}}$.

2.6 Topography

STM topographic images are measured by scanning the tip across the the sample in a square or rectangular pattern. The two raster patterns, x-fast and y-fast, used during measurements for this Thesis are shown in Fig. 2.19. The scans are denoted x-fast or y-fast based upon which direction the lines are measured. This example shows a 512×512 pixel image, the resolution typically used. With the feedback engaged, the tip is scanned along a line parallel to either the x or y direction (line 1). Along this line, the topography is recorded at 512 equally spaced points or pixels. At the end of the line, the tip is scanned back along the same line with another 512 points of topography recorded (line 2). Thus the topography along each line is measured twice, once forward and once in reverse. Once a forward and reverse scan is completed, the tip is moved one pixel in the orthogonal scan direction (3), and the process is repeated. This continues until 512 lines have been measured.

In constant current mode, the feedback mechanism will respond to changes in topography by adjusting the tip height to keep the tunneling current at the current set-point, I_{set} . It does this by varying the voltage applied to the z-direction actuator, V_z . As has been discussed, this actuator is usually a piezoelectric actuator. V_z is recorded at each pixel and changes in topography are calculated using z-axis calibration, A_z . Similarly, the tip lateral position is calculated using the input voltages to the x- and y-axis actuators, V_x and V_y , and the calibration of those actuators, A_x and A_y .

Even with an accurate calibration, the measured topography may not be the true topography if that is defined as the position of atoms at the surface. STM, though,

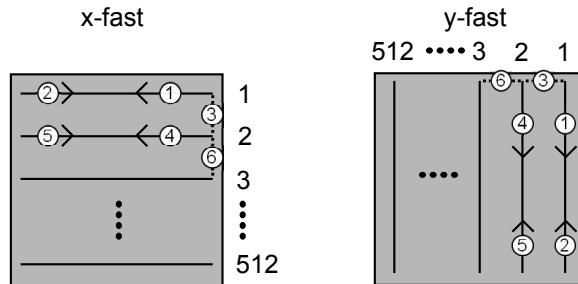


Figure 2.19: Raster scan for STM topography and lock-in conductance map.

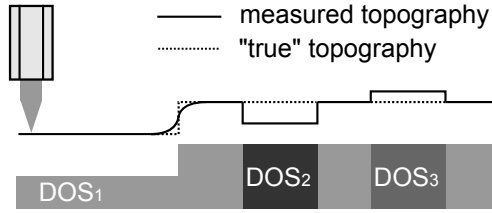


Figure 2.20: STM topography on electronically inhomogeneous sample with step edge.

does not measure the position of surface atoms directly. Instead an STM tip follows a contour of the surface LDOS.^{10,47,48} The tunneling current is a convolution of the tunneling barrier and the tip and sample DOS and is given by,

$$I \propto \int_0^{eV} T(S, V, E) \rho_s(E) \rho_t(E - eV) dE, \quad (2.51)$$

where $T(S, V, E)$ is the tunneling barrier, $\rho_s(E)$ is the sample DOS, and $\rho_t(E - eV)$ is the tip DOS. Usually the tip material is chosen so as to have a flat DOS at the Fermi energy, so Eq. 2.51 reduces to,

$$I \propto \int_0^{eV} T(S, V, E) \rho_s(E) dE. \quad (2.52)$$

Thus the tunneling current is proportional to the integrated sample LDOS within eV of the Fermi energy (E_F). This can have some rather unexpected consequences since it makes the current bias-dependent in a non-trivial way. A well-known example is the 7×7 reconstruction on the Si(111) surface, where the unit cell image is different for different bias voltages.⁴⁹ On the (110) surface of GaAs, only the Ga or the As atoms are revealed in STM topography, depending upon the polarity of the sample bias voltage.⁵⁰ On surfaces with nanometer-scale electronic inhomogeneities, variation in the LDOS can cause features in the measured topography that are the artifacts of electronic variations and not of the true topography. A schematic of a non-homogeneous sample is shown in Fig. 2.20. If, for instance, the DOS is lower in one area of a sample, then the feedback will decrease the tip-sample distance when tunneling in that area, leading to a 'false' dip in the apparent topography.

2.7 Scanning Tunneling Spectroscopy

Mapping the local density of states, LDOS, on material surfaces with an STM is at the core of this research. Information about the LDOS is derived from STS measurements. Two methods to map LDOS predominate in the literature. The first and most complete method is to measure full IV curves at every point. The second method is

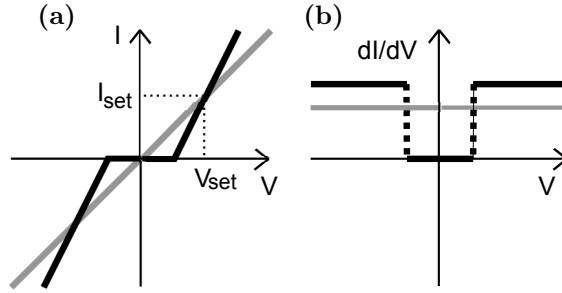


Figure 2.21: Schematic (a) IV and (b) dI/dV curves.

to measure conductance maps with a lock-in amplifier. While a full IV curve maps provide more information, they can be prohibitively time consuming. For this reason, the lock-in method was mostly used in this research.

The full IV method requires that individual IV curves be measured at each point on a grid. Typically the area of interest will be divided up into an n by m grid, with n and m being anywhere from 10 to 64 or more. The tip is scanned over the surface stopping at each point on the grid to measure one or more IV curves. A full map can easily consist of 4096 (64×64) or more IV curves.

Measuring an IV curve begins after the STM tip has been positioned at a particular grid-point. After a short delay to permit any vibrations to decay, the feedback mechanism is disengaged, fixing the tip-sample separation and therefore the tunneling barrier. At this point, with the bias voltage remaining at V_{bias} , the tunneling current will still be I_{set} , the value it was before the feedback was disengaged. Now the bias voltage is swept through a range of voltages, with both the applied voltages and corresponding measured tunneling currents recorded. Schematic IV curves are shown in Fig. 2.21(a).

More than one IV curve is usually measured at each grid point and averaged to reduce white noise. The average IV curve from each grid point is then numerically differentiated to calculate the differential conductance (dI/dV) which is then used as a proxy for the sample LDOS. A schematic dI/dV spectra is shown in Fig. 2.21(b).

In the literature and in this Thesis IV curves are often described as being metallic or insulating, a statement that should be used with care. The tunneling current is a convolution of the sample and tip DOS, and a tunneling transmission probability. Because the tunneling transmission probability can dominate the shape of an IV curve, only curves measured *at the same set-point*—the same V_{bias} and I_{set} —should be compared. Consider the IV curves shown in Fig. 2.21(a). At the set-point, the grey line has a lower conductance yet can be said to be more metallic than the black line, especially since the zero-bias conductance is higher.[†] If they were not measured at the same set-point, then it would be difficult to separate differences due

[†]This can be verified by noting that IV curves measured at the same set-point must intersect at both $V_{\text{bias}} = 0$ and $V_{\text{bias}} = V_{\text{set}}$

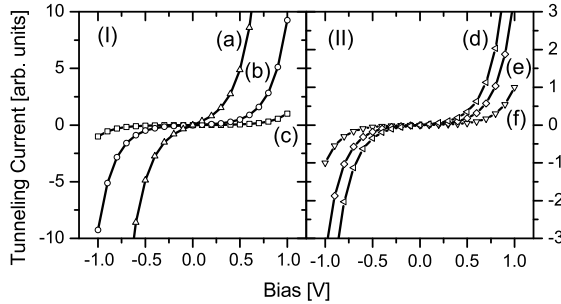


Figure 2.22: Simulated IV curves calculated using Eq. 2.66. (I) The effect of increasing the tip-sample in increments of 1 Å. (II) The effect of varying I_{set} or V_{set} . See text for more detail.

to the differing sample DOS's from those due to the differing tunneling transmission probabilities.

The effect of not measuring IV curves at the same set-point can be illustrated by calculation. Fig. 2.22 shows IV curves calculated using Eq. 2.66 (to be discussed below) for a tip and sample with a flat DOS at E_F and 5 eV average work function, $\bar{\Phi}$. In Fig. 2.22(I), the three curves were calculated with only changes in the tip-sample separation. In curve (a) the tip is closest to the surface while curves (b) and (c) are 1 and 2 Å, respectively, further away. Curve (a) certainly appears more metallic than curve (b) and (c), but the underlying sample DOS used to calculate these three curves is identical, only the tip-sample separation has been modified. Fig. 2.22(II) illustrates the effect of different current and voltage set-points. The effect of a small change in voltage set-point can be seen by comparing curve (d) to curve (e). Both of these curves were calculated with the same current set-point, $I_{set} = 1$, but with differing voltage set-points, $V_{set} = 1.0$ V and $V_{set} = 0.8$ V respectively. The effect of a small change in current set-point can be seen by comparing curve (e) to curve (f). Both of these curves were calculated using the same voltage set-point, $V_{set} = 0.8$ V, but differing current set-points, $I_{set} = 1$ and $I_{set} = 2$ respectively. Even though these curves do not differ in appearance as dramatically as those in Fig. 2.22(I), they still show that small changes in set-point can lead to significant changes in the IV curve. Comparing IV curves or dI/dV spectra measured with different set-points can lead to misinterpreting data, with the effect of different set-point being mistaken for differences in sample DOS. The safest procedure is to only compare IV curves or dI/dV spectra measured at the same set-point.

Although the full IV method gathers a very rich data set, this method can be slow, often prohibitively so. For example, a typical 400 point IV curve requires at least 100 ms to measure. If the tunneling current is noisy, as it was for many of the

samples measured in this work, at every point of a LDOS map, a minimum of 30 to 50 individual IV curves must be measured and averaged to achieve an acceptable signal to noise ratio. Between each IV curve measurement, because of thermal drift, the feedback should be re-engaged for anywhere from 100 ms to 1 s to reestablish the tip-sample distance and therefore I_{set} . Thus, for a relatively low-resolution 64 by 64 grid-point map, the total measurement time would be more than 9 hours. During the measurement, the temperature must be stable and neither the sample nor the tip should degrade. Additionally, any measurement should be repeated, both on each sample and on others. For samples such as the manganites films measured for this Thesis, where measurements were necessary at a series of temperatures and at a series of magnetic fields at each temperature, measuring LDOS maps with full IV curves impractical.

Lock-in conductance maps are made while topography is scanned. The applied bias voltage, V_{bias} , is modulated with a small ac voltage, V_{ac} , at a frequency above the feedback bandwidth. The measured tunneling current will also have an ac component with the same frequency as the bias voltage modulation.[†] The tunneling current is then mixed with V_{ac} using a lock-in amplifier. The output of the lock-in amplifier will be the sample conductance. (Actually the conductance is just the slope of the IV curve at V_{bias} and I_{set} .) This is considerably less information than is contained in a full IV curve, but, nevertheless, can be used to distinguish variations in LDOS on an inhomogeneous sample. Consider the schematic metallic and insulating IV curves shown in Fig. 2.21. At the set point in this illustration, the slopes of the IV curves are different and can be used as an indicator of the LDOS. In any actual measurements, neither the shape of the IV curve nor the significance of a variation in the slope is known *a priori*. The strategy used in this research was to combine lock-in conductance maps with full IV curves taken at selected points. The IV curves provide information about the LDOS, while conductance maps provide information about the spatial variation in electronic structure. When measuring conductance maps the scanning speed is typically less than that used when recording topography alone. This is required because of the limitations imposed by the lock-in amplifier. For every pixel measured the measurement time must be at least three times longer than the time constant of the lock-in filter. The time constant is set based upon the need to filter noise and achieve a stable signal. For the measurements in this Thesis, the time constant was between about 0.1 ms to 30 ms, with 1 ms being typical. For a 512 by 512 pixel conductance map, this would result in a scan time of about 26 minutes. This is considerably less than the time to measure a conductance map with full IV curves, and the reason that lock-in conductance maps were the preferred technique used in this research.

[†]Because the modulation frequency exceeds the feedback bandwidth, the feedback will not respond to this modulation and will operate as if V_{bias} were a dc signal.

2.8 Scanning Tunneling Spectroscopy Theory

The underlying principle of STM is electrons tunneling between a metal tip and a sample through a vacuum barrier. The great sensitivity afforded by the exponential dependence of tunneling current on the tip-sample distance permits the STM tip to be positioned within Å's of the sample surface. STS similarly makes use of vacuum tunneling as a way to position the tip close to the sample surface but also exploits the properties of tunneling to measure the sample DOS. How tunneling can be used to measure the DOS is the subject of this section.

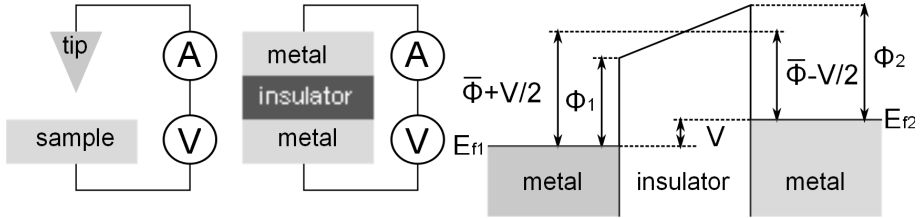


Figure 2.23: Schematic of a NIN planar junction consisting normal metal-insulator-normal metal.

Consider an STM with sample (s) vacuum gap, and tip (t). The current between the tip and sample can be calculated using first-order perturbation theory and is found to be,^{9,47,51–53}

$$I = \frac{2\pi e}{\hbar} \sum_{t,s} [f(E_t - eV) - f(E_s)] |M_{t,s}|^2 \delta(E_t - E_s), \quad (2.53)$$

with $f(E)$ the Fermi function, V the applied voltage between the electrodes, $M_{t,s}$ the tunneling matrix elements between state Ψ_t of the tip and state Ψ_s of the sample, and E_t and E_s are the energy corresponding to these tip and sample states. All that remains is to calculate the tunneling matrix elements, $M_{t,s}$. By using the wavefunctions of the uncoupled tip and sample and then lowest-order perturbation theory, these can be calculated using,^{51,52}

$$M_{t,s} = -\frac{\hbar^2}{2m} \int dS (\Psi_t^* \nabla \Psi_s - \Psi_s^* \nabla \Psi_t), \quad (2.54)$$

with the integral performed entirely within the vacuum between the tip and sample. The electron tunneling between sample (s) and tip (t) can be calculated by assuming the one-dimensional, semiclassical WKB approximation. With this assumption, the tunneling current density is given by, by,⁵³

$$J(S, V) \cong \frac{2\pi e}{\hbar} \left(\frac{\hbar^2}{2m}\right)^2 \int_{-\infty}^{\infty} T(S, V, E) [f(E - eV) - f(E)] \rho_s(E) \rho_t(E - eV) dE, \quad (2.55)$$

where $T(S, V, E)$ is the tunneling transmission probability as a function of barrier thickness, S , applied bias voltage, V , and energy, E ; $\rho_s(E)$ is the sample density of states and $\rho_t(E - eV)$ is the tip density of states; and $f(E)$ is the Fermi function. At temperatures typical for STM, the Fermi function can be approximated as a step function and so (2.55) can be simplified to,

$$J(S, V) \cong \frac{2\pi e}{\hbar} \left(\frac{\hbar^2}{2m} \right)^2 \int_0^{eV} T(S, V, E) \rho_s(E) \rho_t(E - eV) dE. \quad (2.56)$$

Assuming a trapezoidal barrier, the tunneling transmission probability can be written in the semiclassical WKB approximation, as,

$$T(S, V, E) \cong \exp \left\{ -2S \left(\frac{2m}{\hbar^2} \left[\bar{\Phi} + \frac{eV}{2} - E \right] \right)^{1/2} \right\}, \quad (2.57)$$

where $\bar{\Phi}$ is the average of the sample and tip work functions. The next step would be to calculate the tunneling current from (2.56), but as will become apparent, it is easier to extract the sample DOS from the differential conductance. Differentiating (2.56) with respect to bias voltage gives the differential conductance,

$$\begin{aligned} \frac{dI(S, V)}{dV} &\cong A \left[eT(S, V, E) \rho_s(E) \rho_t(E - eV) \right]_{E=eV} \\ &\quad + \int_0^{eV} T(S, V, E) \rho_s(E) \frac{d\rho_t(E - eV)}{dV} dE \\ &\quad + \int_0^{eV} \frac{dT(S, V, E)}{dV} \rho_s(E) \rho_t(E - eV) dE \Big], \end{aligned} \quad (2.58)$$

where A is a constant proportional to the effective sample-tip area. But we still cannot solve for $\rho_s(E)$ in (2.58) and further simplifying assumptions must be made. Because the tip is usually chosen to be a metal with a constant DOS E_F the second term in (2.58) can be neglected. From here there are a number of ways to proceed. Perhaps the most common way is to assume that at low bias voltages $T(S, V, E)$ is constant and the third term in (2.58) can be neglected. Given these assumptions, the tunneling current can be written as,^{54,55}

$$I \propto \int_0^{eV} T(E) \rho_s(E) dE, \quad (2.59)$$

and the differential conductance can be written as,

$$\frac{dI}{dV} \approx eT(eV) \rho_s(eV). \quad (2.60)$$

Using these two equations we can calculate the normalized conductance,

$$\frac{dI/dV}{I/V} \approx \frac{eT(eV) \rho_s(eV)}{1/V \int_0^{eV} T(E) \rho_s(E) dE} + \dots \quad (2.61)$$

To a first order, the transmission probability can be canceled from the numerator and denominator and this reduces to,

$$\frac{dI/dV}{I/V} \approx \frac{\rho_s(eV)}{1/eV \int_0^{eV} \rho_s(E) dE}. \quad (2.62)$$

In this equation the denominator can be considered a normalization constant, and so,

$$\frac{dI/dV}{I/V} \propto \rho_s(eV). \quad (2.63)$$

Thus the differential conductance normalized by the total conductance is proportional to the sample density of state. In practice, the normalized conductance is calculated from the measured IV curve by dividing the numerical derivative of the tunneling current by the tunneling current at that bias and then multiplying by the bias,

$$\left. \frac{dI/dV}{I/V} \right|_{V_i} \approx \frac{\Delta I_i / \Delta V_i}{I_i / eV_i}. \quad (2.64)$$

This method cannot be used directly on samples with a gapped DOS as the measured current will be zero at non-zero bias voltages and the normalized conductance will diverge. To avoid divergence on insulating or semiconducting samples, the function I/V is smoothed or broadened by convoluted it with a suitable function. One function used for broadening is the exponential function,

$$\overline{I/V} = \int_{-\infty}^{\infty} (I/V') \exp\left[\frac{V' - V}{\Delta V}\right] dV'. \quad (2.65)$$

Broadening using this method can distort the normalized conductance if the convolution is too broad. Another issue is caused by noise in the current signal. At small currents, the noise can be of the same order of magnitude as or larger than the signal. Dividing by a small and noisy current leads to an extremely noisy normalized conductance. Averaging multiple curves can alleviate this somewhat, but not completely, whereas curve smoothing can distort the normalized conductance. Because of these issues, noise can be a particular problem if either qualitative or quantitative details of the band gap edge are important.

A second method uses a non-linear fit of the tunneling barrier to extract the sample DOS.⁵³ The tunneling transmission probability is no longer assumed to be a constant, and thus the third term in (2.58) is not neglected. Substituting $\xi = (E - eV/2)$ into (2.58) and (2.57) will make them symmetric with respect to the tip and sample DOS.

This gives,

$$\begin{aligned}
\frac{dI(S, V)}{dV} \cong & \frac{Ae}{2} \left[T'(S, \xi) \rho_s(\xi + eV) \rho_t(\xi - eV) \Big|_{\xi=eV/2} \right. \\
& + T'(S, \xi) \rho_s(\xi + eV) \rho_t(\xi - eV) \Big|_{\xi=-eV/2} \\
& + \int_{-eV/2}^{eV/2} T'(S, \xi) \frac{d\rho_s(\xi + eV)}{dV} \rho_t(\xi - eV) d\xi \\
& \left. + \int_{-eV/2}^{eV/2} T'(S, \xi) \rho_s(\xi + eV) \frac{d\rho_t(\xi - eV)}{dV} d\xi \right], \tag{2.66}
\end{aligned}$$

and

$$T'(S, \xi) \cong \exp \left\{ -2S \left(\frac{2m}{\hbar^2} [\bar{\Phi} - \xi] \right)^{1/2} \right\}. \tag{2.67}$$

Once again we assume that the tip DOS is constant at E_F , eliminating the fourth term in (2.66). At this point in the analysis, consider only tunneling between two metals. Since the DOS for a metallic sample is also flat then the third term in (2.66) would be eliminated. What remains is an equation that models tunneling between two metallic conductors with flat DOS's. The differential conductance is now,

$$\begin{aligned}
\frac{dI(S, V)}{dV} \cong & \frac{Ae}{2} \left[T'(S, \xi) \rho_s(\xi + eV) \rho_t(\xi - eV) \Big|_{\xi=eV/2} \right. \\
& \left. + T'(S, \xi) \rho_s(\xi + eV) \rho_t(\xi - eV) \Big|_{\xi=-eV/2} \right], \tag{2.68}
\end{aligned}$$

or equivalently,

$$\begin{aligned}
\sigma(S, V) \equiv \frac{dI(S, V)}{dV} = & \frac{Ae}{2} \left[\exp \left\{ -2S \left(\frac{2m}{\hbar^2} [\bar{\Phi} - eV/2] \right)^{1/2} \right\} \right. \\
& \left. + \exp \left\{ -2S \left(\frac{2m}{\hbar^2} [\bar{\Phi} + eV/2] \right)^{1/2} \right\} \right]. \tag{2.69}
\end{aligned}$$

If we now compare this curve to the differential conductance between a metallic tip and a non-metallic sample, we can take the difference between them as representing the sample DOS scaled by a constant. In practice, a non-linear fit is made of (2.69) to the high-bias part of $\Delta I/\Delta V$, the numerical derivative of the IV curve, with fit parameters A , S , and $\bar{\Phi}$. The deviation of $\Delta I/\Delta V$ from the fitted curve is the sample DOS. At high bias they should be identical, but at low bias, where the sample DOS could be gapped or depleted, there will be a difference. The advantage of this method over the first method described is that the procedure does not involve dividing by the tunneling current and thus avoids dividing by what can be a small number.

Unfortunately, this method is not without problems. As there are three fit parameters and fits to experimental data can lead to widely varying values. Another weakness is that for the procedure to work, the sample DOS must be flat at high bias values where the fit is to be made.

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.⁵⁶ 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.⁵⁷ 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, $RE_{1-x}A_x\text{MnO}_3$, 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 $RE\text{MnO}_3$ and $A\text{MnO}_3$, with electronic configurations Mn^{3+} and Mn^{4+} respectively.⁵⁹ 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.⁵⁸ 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.

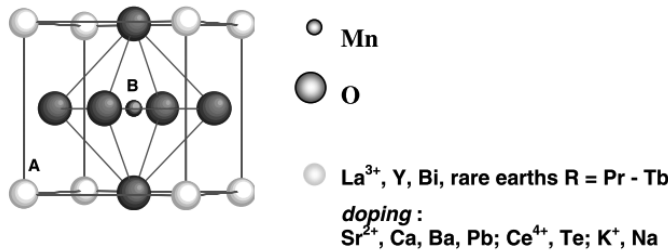


Figure 3.1: Manganite pseudo-cubic perovskite structure of type ABO_3 . Taken from Ref. 58

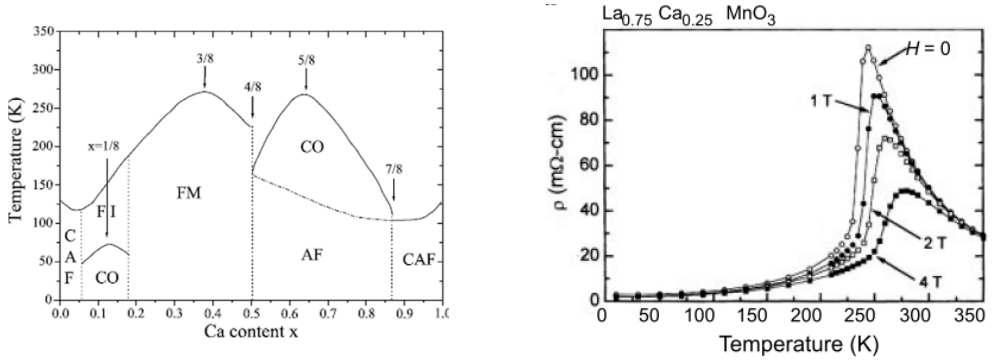


Figure 3.2: (Left) Phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. Taken from Ref. 60. (Right) Resistance versus temperature for $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$. Taken from Ref. 56.

The particular manganite studied here is Ca-doped LMO or $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. 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 $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is shown in Fig. 3.2 (left). At elevated temperatures—in the unlabeled portion of the diagram— $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ 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).[†] Measured resistivity (ρ) as a function of temperature (or RT)[‡] for close to optimally doped $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ 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 $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ 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

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

[‡]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.

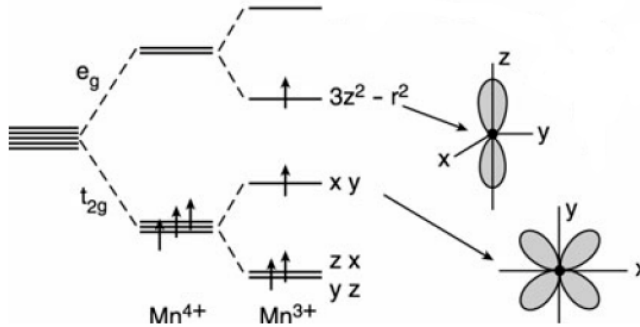


Figure 3.3: Crystal field and Jahn-Teller splitting for Mn^{3+} and Mn^{4+} ions. Also shown are $4d$ orbitals with apical oxygen stretching. Taken from Ref. 61

above T_p is described as insulating (meaning $dR/dT < 0$).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 $3d$ orbital (see Fig. 3.3). The electrostatic interaction of the Mn $3d$ orbital with the oxygen $2p$ orbitals creates a crystal field. This interaction splits the five-fold degenerate $3d$ 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.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 octahedron 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.^{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 Θ 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 coexist 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 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.^{66–71} 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.^{72–81}

Nevertheless, from STM and STS measurements of thin-film manganites, evidence of half-metallicity,⁸² polarons,^{69,82} and pseudo-gaps⁸³ have all been claimed, while spatial electronic PS has been mapped as a function of both applied magnetic field,^{66,68} and temperature.⁶⁷ 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 $\text{La}_{1-x}\text{Sr}_x\text{MnO}$ or narrower bandwidth systems such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$; or for differing strain states such as fully strained versus (partially) relaxed.

3.2 Experiment

We confined our STM/STS study to thin-film $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. 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

[†]The pseudocubic lattice parameters for bulk $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, NdGaO_3 , and SrTiO_3 are ~ 3.86 Å, ~ 3.863 Å, and ~ 3.905 Å respectively.⁵⁸

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 SrTiO₃(001) and NdGaO₃(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 *in-situ*, immediately after sputtering. Others were annealed *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 α_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 α_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 O₂ and Ar at a calibrated etch rate of 1 nm/minute. This combination has been shown to etch SrTiO₃ 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 4×10^{-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_{set}) and current (I_{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_{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.

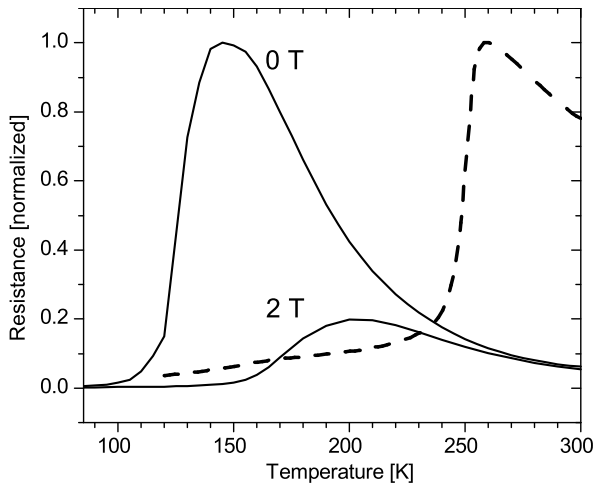


Figure 3.4: Resistance versus temperature curves normalized to the zero-field peak resistance. The solid curve is of a 10 nm $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on SrTiO_3 , measured in the indicated magnetic fields ($T_p \approx 145$ K). The dashed curve is of a 26 nm $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on NdGaO_3 ($T_p \approx 260$ K).

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, ≈ 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.

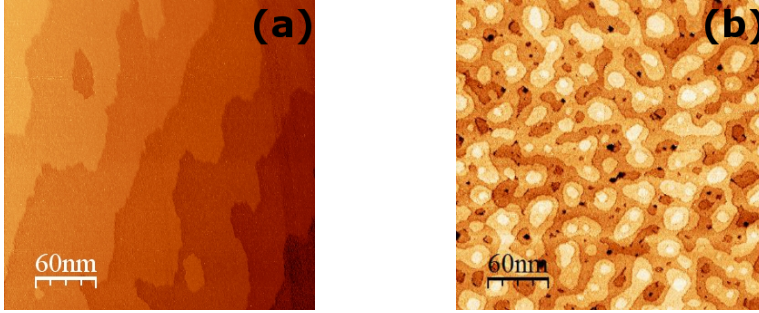


Figure 3.5: Ambient STM images of typical terraced, (a), and island, (b), topography for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ grown on SrTiO_3 substrates. Films are 10 nm thick. Both images exhibit unit-cell step heights.

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 ($T_p \approx 145$ K) and unstrained films grown on NGO ($T_p \approx 260$ 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 (≈ 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 6.5×10^{-11} to 6.1×10^{-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 is shown in (a). The surface is rough, with peak-to-peak height variations of ≈ 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,

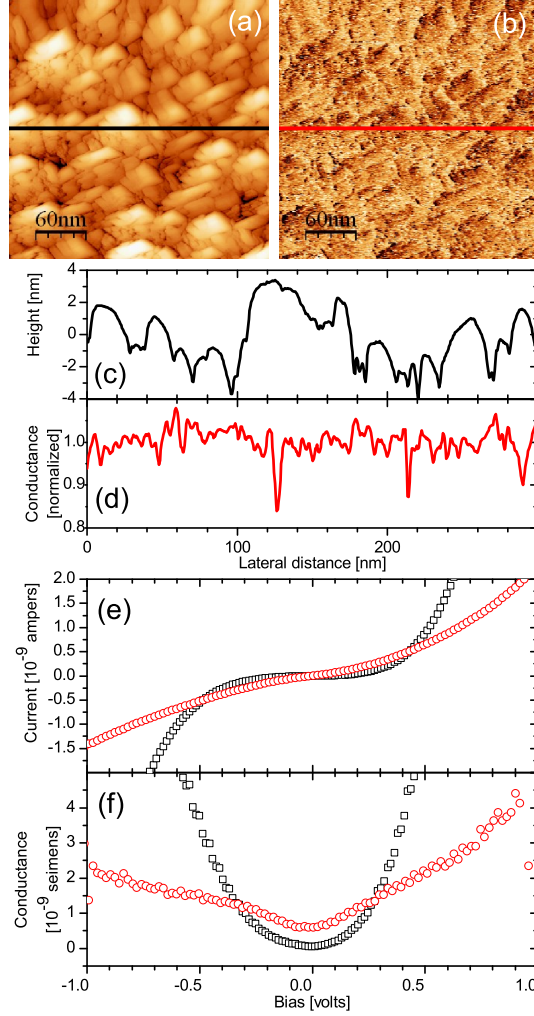


Figure 3.6: STM measurements of a rough 50 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on NdGaO_3 . Its peak temperature T_p is 260 K. (a) Topography, (b) conductance map, (c) section through topography, and (d) normalized section through conductance map. Measured simultaneously at 280 K in zero magnetic field. $V_{set} = -0.5$ V, $I_{set} = 0.5$ nA, and $V_{ac} = 10$ mV. (e) I - V measurement and (f) corresponding dI/dV spectra. Measured at 299 K at different locations on the film. $V_{set} = -0.5$ V, $I_{set} = 0.5$ nA, $V_{sweep} \pm 1$ V. All measured in Helium gas.

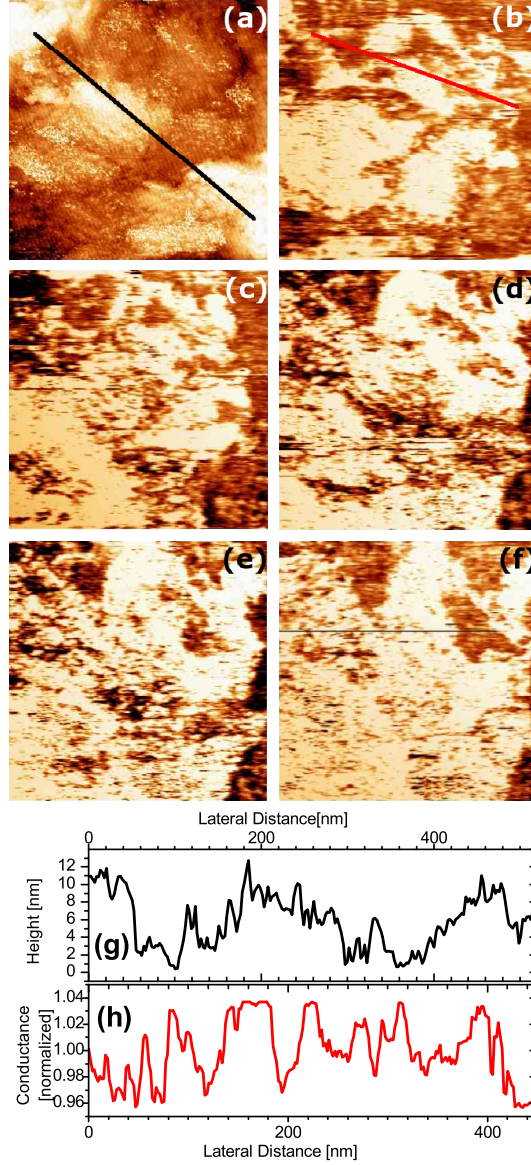


Figure 3.7: STM measurements of a rough 100 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on Nb-doped SrTiO_3 substrate. Its peak temperature T_p was about 250 K. All images are 500 nm^2 . Topography is shown in (a). Conductance maps with applied magnetic fields of 0, 2, 4, 6, and 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), $V_{\text{set}} = -2.0 \text{ V}$, $I_{\text{set}} = 0.2 \text{ nA}$, and $V_{\text{ac}} = 24 \text{ mV}$.

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

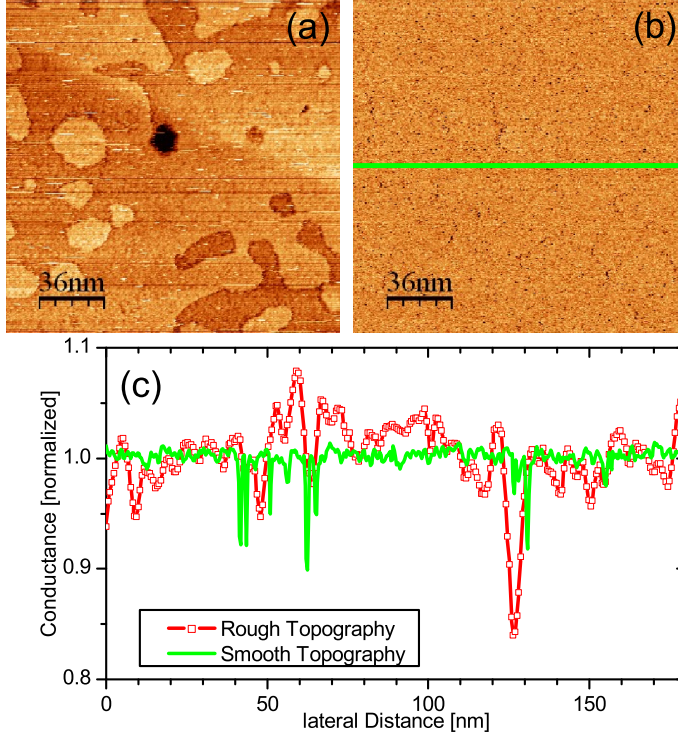


Figure 3.8: STM measurements of atomically smooth 10 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on SrTiO_3 . Its peak temperature T_p was about 145 K. (a) Topography and (b) conductance map. Measured in helium gas at 150 K with zero magnetic field. The height between terraces matches unit-cell size. $V_{\text{set}} = -3.0$ V, $I_{\text{set}} = 3.0$ pA, $V_{\text{ac}} = 8.0$ mV. (c) Normalized section through conductance maps of this film (green) and the rough film from Fig. 3.6 (red).

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 $V_{\text{set}} = -3.0$ V, but other measurements with V_{set} as low as 0.1 V were substantially the same, though with more pronounced feedback-error features. Conductance maps taken at temperatures above and below the MIT were also featureless, as were those made in an applied field. Measurements made on other flat LCMO films whether grown on STO or NGO, or whether measured in the UHV or gas-flow STM were similarly homogeneous, regardless of temperature or magnetic field.

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

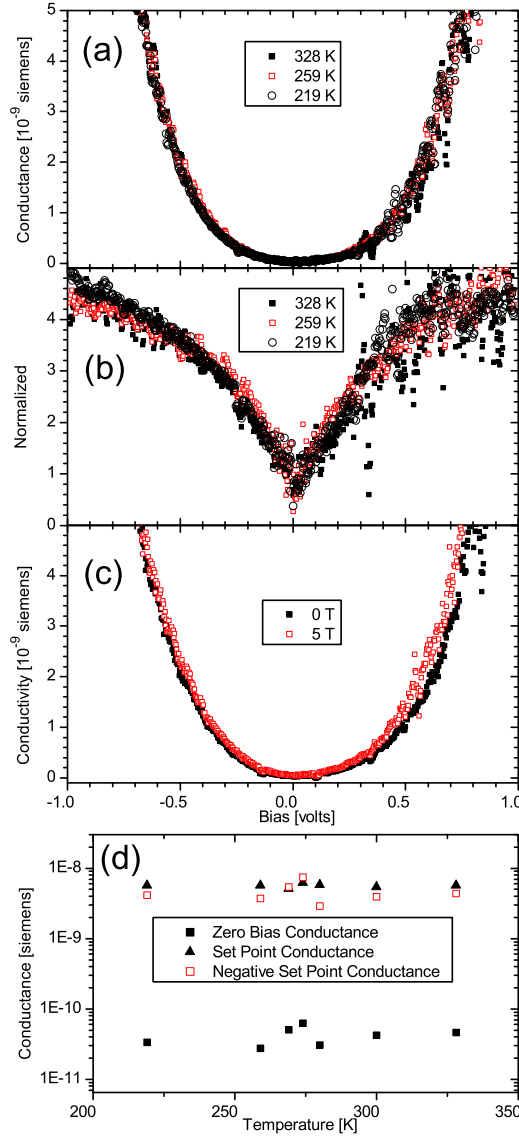


Figure 3.9: STS measurements of a smooth 26 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on NdGaO_3 . Its peak temperature T_p was 260 K. (a) Numerically differentiated I - V curves in zero magnetic field at indicated temperature. (b) Spectra from (a) normalized by dividing through 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.

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 1.5×10^{-9} to 3.5×10^{-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-metallicity⁸² 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.

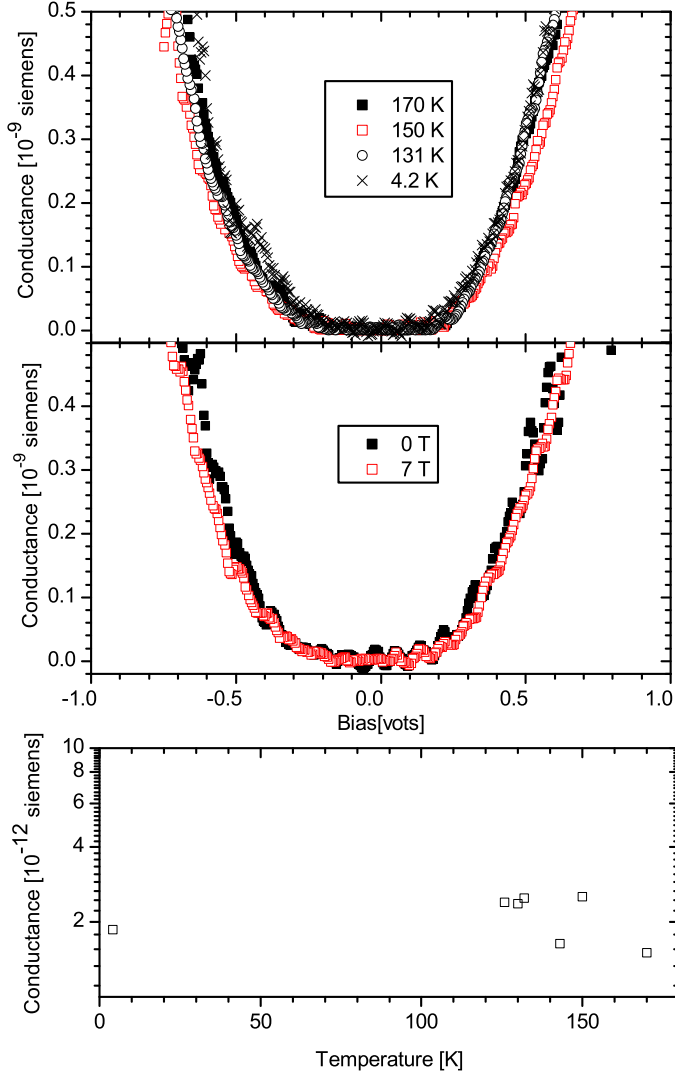


Figure 3.10: STS measurements of a smooth 10 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on SrTiO_3 . Its peak temperature T_p was 145 K. Numerically differentiated I - V curves (a) in zero magnetic field at indicated temperature and (b) at 121 K at indicated magnetic field. (c) Conductivity calculated from numerically differentiated I - V curves in zero magnetic field. $V_{set}=1.0$ V, $I_{set}=0.5$ nA, $V_{sweep}\pm 1.0$ V. Measured in UHV.

Similar results were seen on flat films grown on STO. Fig. 3.10 shows dI/dV spectra measured on a 10 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ 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.*,⁸⁸ 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—what 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 1×10^{-6} mbar. Beyreuther *et al* found below-stoichiometry oxygen in manganite films exposed to UHV at elevated temperatures (470-670°C),⁸⁷ 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

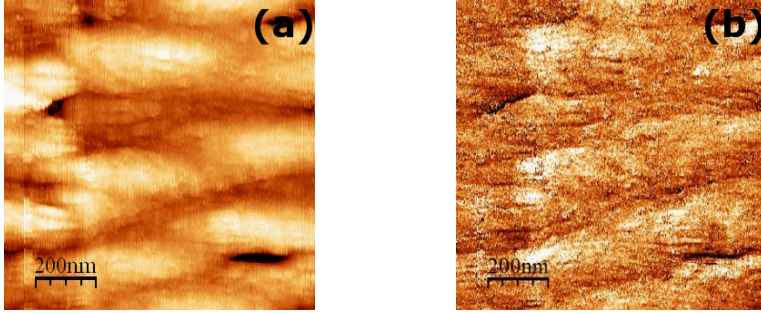


Figure 3.11: STM image of an annealed 26 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on NdGaO_3 after annealing at 470°C for 3 hours in flowing oxygen. (a) Topography and (b) conductance map. Measured in ambient.

also electronically inhomogeneous. In contrast, before annealing, the film exhibited 2-D island growth with a homogeneous conductance map. Our experiments with oxygen annealing suggest two possibilities. Oxygen annealing does lead to an active surface layer, but, coincidentally, the film roughens at about the same temperature. Alternatively, it is the roughening of the film's surface that leads to an active surface layer, and the oxygen is only necessary to avoid further de-oxidizing of the film.

3.4 Discussion

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.⁶⁶ Another publication reports PS and field-induced percolation, but on a flat film.⁸⁹ Other researchers report PS on a rough film, but find that an applied field induces an overall increase in conductivity, not percolation.⁹⁰ Finally, a number of researchers report electronically homogeneous films that, unlike our flat films, are electronically active. These homo-

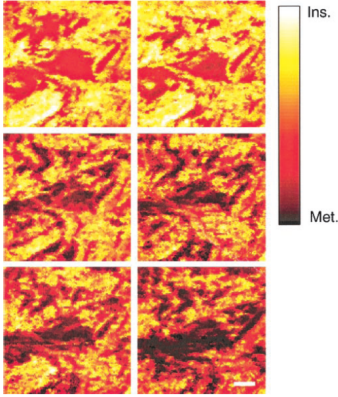


Figure 3.12: Effect of magnetic field on rough $\text{La}_{0.7}\text{Cr}_{0.3}\text{MnO}_3$. $610 \times 610 \text{ nm}^2$ conductance maps in magnetic fields 0, 0.3, 1, 3, 5, and 9 T (from left to right and top to bottom).⁶⁶

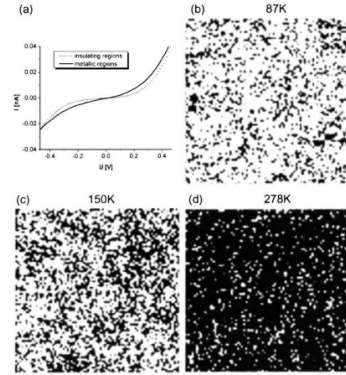


Figure 3.13: Effect of changing temperature on rough $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. (a) Typical I-V curves from metallic and insulating regions. (b)-(d) $500 \times 500 \text{ nm}^2$ conductance maps at indicated temperature.⁶⁷

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.⁶⁶ 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-

sented by Becker *et al.* They measured zero-bias conductance (ZBC) maps[†] of both an LCMO film and a $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ 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 *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 *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 *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

[†]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.

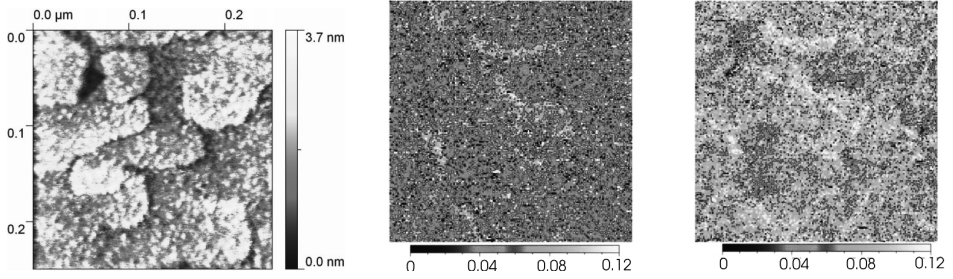


Figure 3.14: Topography and STS from Köster *et al* on a layer-by-layer grown LCMO film.⁹⁰ Topography (left). STS of the same film measured at 267 K ($T_p = 270$ K). Measured in zero field (center) and 4 T (right). All images $250 \times 250 \text{ nm}^2$.

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.^{90,93} In one publication Moshnyaga *et al* measured LCMO films on MgO at 115 K, significantly below the film's MIT temperature.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.[†] 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 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 .⁹⁰ They detect PS on both films, though the PS was more pronounced on the

[†]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).

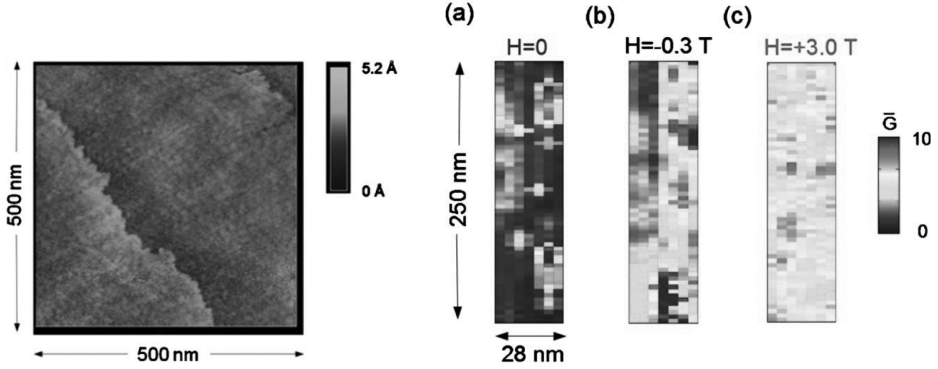


Figure 3.15: Topography and STS from Hughes *et al* of terraced LCMO film.⁸⁹ Topography (left). STS of the similar film measured at 6 K (T_p 270 ± 10 K). Measured in (a) zero field, (b) -0.3 T, and (c) 3 T.

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.⁸⁹ 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 their use of high-bias STS allows them to probe through a surface dead

[†]Perhaps 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.

layer, allowing them to see PS where others have not. This is certainly true of their own measurements; their low-bias conductance maps were more homogeneous than their high-bias conductance maps.

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 $\text{Mn}^{3+/4+}$ 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 $\text{Mn}^{3+/4+}$ 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 $\text{Mn}^{3+/4+}$ 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-

sistance 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.^{100,101} Relevant in this respect are data taken on microbridges of thin (10 nm) strained films of LCMO on STO.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 $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$, with a doping closer to the FI part of the doping phase diagram.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 (μ).¹⁰⁴ In contrast, a hard gap would have a range of energies about μ 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,^{83,89,105–107} describing their data in terms of in terms of a pseudogap width (Δ) or a zero bias conductance (ZBC) or both. Mitra *et al.*,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

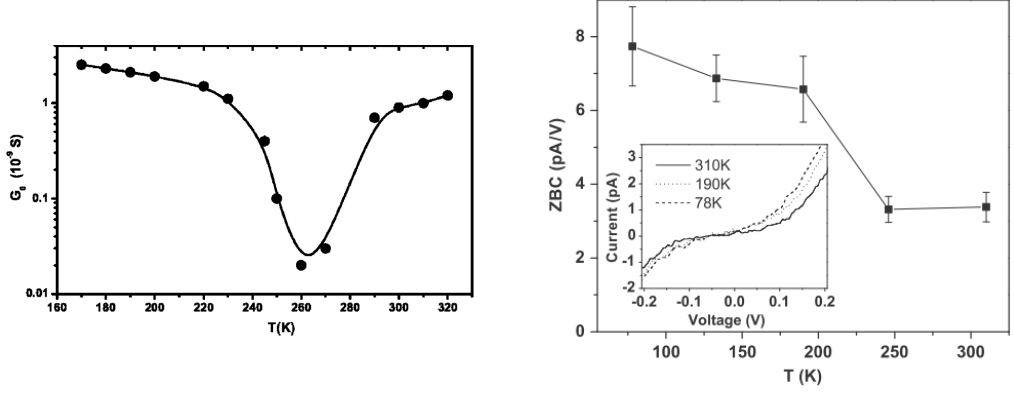


Figure 3.16: (Left) Plot of G_0 (or ZBC) from Mitra *et al.*⁸³ (Right) Plot of ZBC from Singh *et al.*¹⁰⁷

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.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 dI/dV spectra measured at 300 K but found that the pseudogap varied across the sample surface.⁸⁹ In the research reported here, the variation in ZBC on LCMO/NGO films varied little, ranging from between about 1.8×10^{-11} to 5×10^{-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 dI/dV 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).

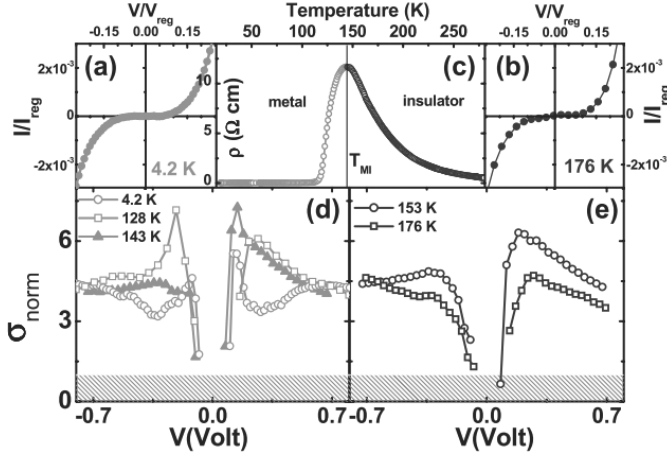


Figure 3.17: STS measurements on atomically smooth LCMO film grown on STO. (a) and (b) Plots of IV s measured at indicated temperatures. (c) Resistivity from transport measurement. (d) and (e) Normalized dI/dV s. Taken from Ref. 69

Polarons-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 $\rho(T) \approx \rho_0 T^\alpha \exp(\frac{E_a(T)}{k_B T})$ 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,^{69,107–113} although there has been at least one report of best-fit to the non-adiabatic SP.¹¹⁴ 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.⁶⁹ 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 .¹⁰⁷ In one of the first STS measurements of LCMO, Wei *et al.* found evidence of polaron peaks (energy gap ~ 0.5 eV) but only at 77 K, well below T_c .⁸² 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.^{69,83} 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.^{69,83} Considering the difficulty of separating sample DOS from the tunneling barrier,^{53,85} 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,⁵⁴ 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.^{76,77,96,115} Other research has shown that the oxygen content at the film surface is very sensitive to elevated temperatures, whether in oxygen or UHV,^{87,116} or to prolonged air exposure.¹¹⁷ 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.⁷⁹ Because we did not directly measure the surface oxygen

[†]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.

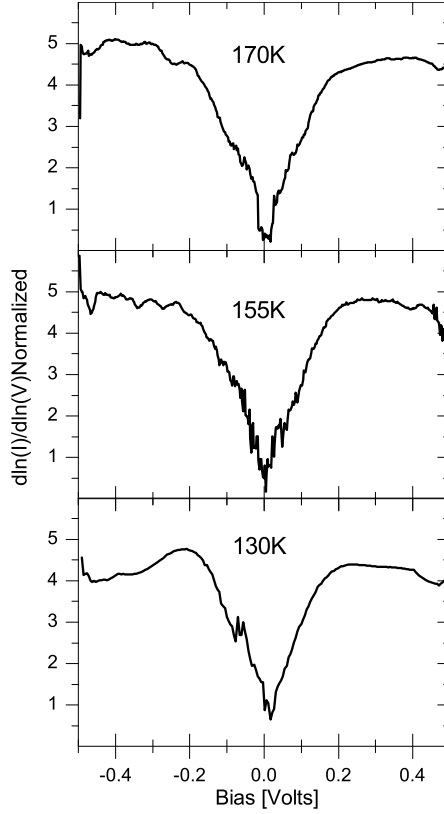


Figure 3.18: (Color online) Numerically differentiated and normalized I - V curves of smooth 52 nm thick $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on SrTiO_3 $T_p \approx 155$ K. $I_{set}=0.5$ nA, $V_{set}=0.5$ V, $V_{sweep} = \pm 0.5$ V. Measured in UHV at indicated temperatures with 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,⁶⁹ rapid transfer to STM followed by rapid cool to low temperature,⁶⁷ isopropanol cleaning followed by heating to 150 C in air,⁹⁰ 24 hour bake in high vacuum,¹⁰⁵ and cleaning in 0.5% Br in ethanol.⁸⁹ 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*.¹¹⁸ 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 annealing 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 stoichiometry 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^{66,67} and smooth^{89,90,93} films, while electronic homogeneity has only been detected on smooth films,^{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 ,⁷⁰ another report on a similar sample found only a homogeneously distributed FM phase.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,^{69,82} or even a pseudogap without coherence peaks.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,⁸² while in another coherence peaks are a fixture at all temperatures.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.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,¹¹⁹ isotope-effect,¹²⁰ and at least one resistivity measurement¹²¹—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,⁶⁹ or the gap width at half depth.¹⁰⁷ One group measured an almost monotonic increase in binding energy with decreasing temperature,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 .⁶⁹ In comparison, binding energy extracted optical conductivity increased monotonically with temperature until plateauing above T_c .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.

Chapter 4

Cobaltites

In the previous Chapter, manganite thin films were studied by STM in order to find the spatial scales on which the material is inhomogeneous. Although the surface sensitivity of the technique can be a problem, STM has the advantage over other techniques that it can provide real-space information, but also that that measurements can be made on thin films, where other real space techniques are limited.

Another materials system where electronic phase separation is thought to be important is the cobalt-based perovskite $R_{1-x}A_x\text{CoO}_3$, in which R and A are again a trivalent Rare-Earth and a divalent alkaline ion, respectively. In the following we concentrate on $(\text{La,Sr})\text{CoO}_3$ (LSCO). Much like manganites, doping leads to a mixture of Co^{3+} and Co^{4+} ions, but otherwise the two materials are quite different, mainly due to the different spin states of the Co ion. In particular, for $x > 0.2$, the material is a metallic cluster ferromagnet, in contrast to e.g $(\text{La,Sr})\text{MnO}_3$, which is a homogeneous ferromagnet. Similarly, for $x < 0.2$ it becomes a semiconducting spin glass, whereas manganite becomes an insulating ferromagnet. The spin glass state consists of nano-sized ferromagnetic clusters in a non-magnetic matrix, and thereby is an example of a phase-separated state (sometimes called magneto-electronic phase separation or MEPS).

Thin films add the usual issues of strain and oxygen stoichiometry to the question of the magnetic and electronic state of LSCO, and can show a large variety of properties. A very interesting example is the thickness dependence of films with the composition $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, which in bulk form is the well-behaved cluster ferromagnet mentioned above. Growing them slightly strained on SrTiO_3 , the films have a suppressed saturation magnetization and are insulating below a critical thickness (t^*) of about 5-8 nm, but switch to bulk-like behavior above t^* .^{123,124} The reason for this crossover is not yet clear, and we have used STM to characterize the small-scale properties of two such films, one of ~ 4.7 nm (below t^*), and one of ~ 12.4 nm (above t^*). Also in the STM data, the behavior of both films is strikingly different, as will be discussed.

The Chapter starts with a discussion of the physics of the $(\text{La,Sr})\text{CoO}_3$ system in Section (4.1), and of the behavior of films with $x = 0.5$ in Section 4.2. Some brief remarks on the experimentation are made in Section 4.3, followed by a presentation (Section 4.4), and discussion of this data (Section 4.5).

4.1 Introduction

The parent compound of LSCO is LaCoO_3 (LCO). LCO is a pseudocubic perovskite, with the Co ions contained within an O octahedron. The crystal field of the O octahedron lifts the five-fold degeneracy of the Co 3d orbital, lowering the energy of the triply-degenerate t_{2g} orbital with respect to the energy of the doubly-degenerate e_g orbital. The e_g orbital has a higher energy due to Coulomb repulsion since its orbital lobes point towards the O ions forming the octahedron.¹²⁵

The crystal-field splitting (CFS) in LCO has a strong influence on the properties of the cobaltites. This stems from the similar energy scale of the crystal field energy (E_{cf}) and the intra-atomic exchange energy (E_{ex}). In a simple picture of LCO as an ionic compound, the ions are in the O^{2-} , La^{3+} , and Co^{3+} states. In this charge state, Co^{3+} will have six 3d electrons, and, in an isolated ion, Hund's rules would lead to a $S=2$ spin state. This is illustrated on the far left side of Fig. 4.1. In a weak crystal field ($E_{cf} \leq E_{ex}$), the ground state will have all six electrons paired up in the t_{2g} orbital, leaving the Co^{3+} ion in a low spin (LS) state with $S=0$ ($t_{2g}^6 e_g^0$). With the relative increase of E_{cf} over E_{ex} , Co^{3+} is promoted to the intermediate spin (IS), or high spin (HS) state, as illustrated in Fig. 4.1.

In LCO, the Co ion is in an LS state at low temperature (T). As the temperature is raised, LCO will go through a number of transitions. At about 90–100 K, thermal excitations will overcome E_{cf} and electrons will be promoted to the e_g orbital and produce either an IS state with two unpaired electrons and spin $S=1$ ($t_{2g}^5 e_g^1$) or a HS state with four unpaired electrons and spin $S=2$ ($t_{2g}^4 e_g^2$).^{127–129} At temperatures above this spin-state transition, the susceptibility is consistent with Curie-Weiss behavior and LCO is paramagnetic.¹²⁷ Below 500 K, transport measurements indicate that LCO is an insulator, with resistivity diverging as $T \rightarrow 0$ K. At ~ 500 K LCO undergoes a phase transition and is a poor metal at higher temperatures.

Sr doping introduces a variety of new properties to LCO. The magnetic phase diagram of LSCO is shown in Fig. 4.2.¹²⁶ With changes in temperature and doping

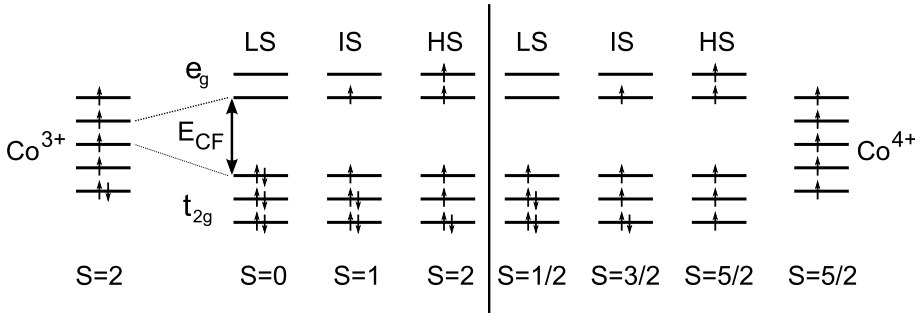


Figure 4.1: Illustration of Co^{3+} and Co^{4+} spin states in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. LS stands for low spin, IS for intermediate spin, and HS for high spin. Adapted from Ref. 126

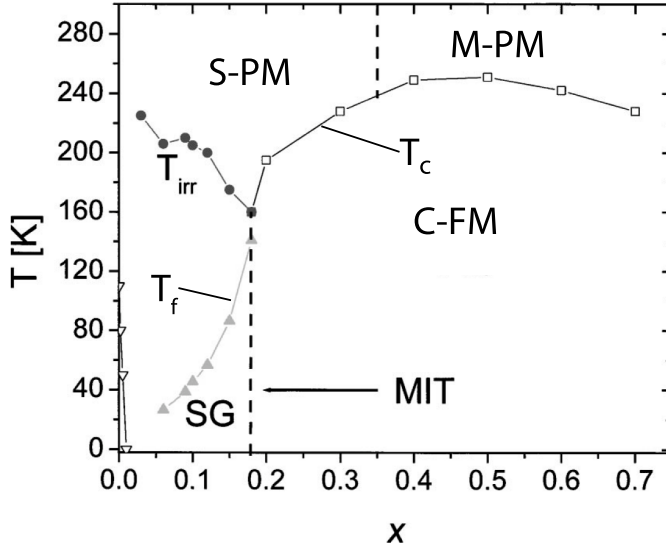


Figure 4.2: Temperature-magnetism phase diagram of bulk $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. Acronyms are defined in the text. Taken from Ref. 126

LSCO produce various phases including a cluster ferromagnetic metal (C-FM), a spin glass (SG), a paramagnetic metal (M-PM), and a paramagnetic semiconductor (S-PM). At Sr-doping $x_c \sim 0.18$, LSCO undergoes a metal to insulator (MIT) transition from an insulator for $x < 0.18$ to a metal for $x > 0.18$. Further details of this phase diagram and supporting evidence is discussed below.

The effect of Sr-doping $0 < x < 1$ is to introduce a mixed Co^{3+} and Co^{4+} state. With doping, a divalent Sr ion, Sr^{2+} , will substitute for a trivalent La^{3+} , and convert Co^{3+} to Co^{4+} . This change will have a significant effect on the spin state of the Co ion. As in the case of Co^{3+} , because E_{cf} still dominates E_{ex} , all of the Co^{4+} ions 3d electrons will reside in the t_{2g} orbital (see right side of Fig. 4.1). Now there are only 5 electrons, and the LS state of Co^{4+} will have a net spin of $S=1/2$ with occupancy $t_{2g}^5 e_g^0$.¹²⁶

There is evidence, however, indicating that the ground state for LSCO in the C-FM phase is not simply a mix of LS Co^{3+} ($S = 0$) and LS Co^{4+} ($S = 1/2$), with S between 0 and $1/2$ in proportion to the relative fraction of Co^{3+} and Co^{4+} . Below T_c it has been shown that the best fit of the Brillouin function to magnetization measurements is one with $S \sim 1.25$. Furthermore, above T_c , the best fit to the Curie-Weiss law is with $1 < S < 1.25$. This evidence points to the spin state of C-FM phase LSCO being a mix of IS Co^{3+} with $S=1$ and IS Co^{4+} with $S=3/2$. That Co^{3+} and Co^{4+} are not in the LS state is a consequence of the IS state being stabilized by the hybridization of Co and O orbitals.¹²⁶

Regardless of the spin state, the presence of both Co^{3+} and Co^{4+} ions enables

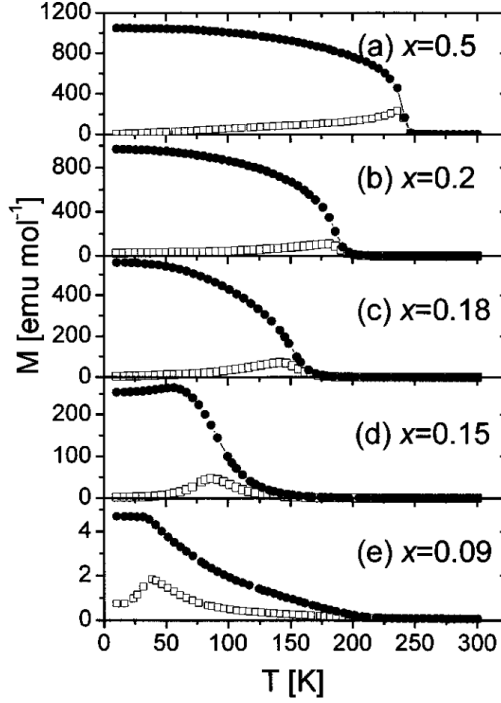


Figure 4.3: ZFC (closed circle) and FC (open square) dc magnetization versus temperature of bulk $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ at various doping levels. Field cooling in 10 Oe. Taken from Ref. 126

double exchange. Double exchange promotes the alignment of adjacent Co^{3+} and Co^{4+} core-spins and, thus, ferromagnetism. Without mixed valence, Co^{3+} or Co^{4+} ions would be stabilized by superexchange into an AFM spin orientation.

With doping between ~ 0.18 and 0.7 , the ground state of LSCO is a cluster FM. Evidence for this comes from a variety of measurements, including dc magnetization. In the doping range $x > x_c$ field-cooled (FC) temperature-dependent magnetization measurements have the characteristic Brillouin-like form of a ferromagnet.^{126,130} An example from the literature of dc magnetization for a selection of doping levels is shown in Fig. 4.3.¹²⁶ While the FC magnetization (solid circle) appears Brillouin-like for $x \geq 0.18$, the FC magnetization at lower doping is not.

The zero-field cooled (ZFC) magnetization data for $x > 0.18$, however, is not characteristic of a model ferromagnet and is non-monotonic and peaked a few Kelvin below T_c . This behavior is typically associated with a ferromagnetic cluster model. In this model, the LSCO separates into Co^{4+} -rich clusters surrounded by a Co^{4+} -poor matrix. Within the clusters, the mixed valence enables oxygen-mediated double exchange ($\text{Co}^{4+}\text{-O-Co}^{3+}$) producing intra-cluster ferromagnetism. Within the Co^{4+} -

poor matrix though, oxygen-mediated super exchange between neighboring Co^{3+} ions will produce an antiferromagnetic matrix.¹²⁶

The peak in the ZFC magnetization data is interpreted as a competition between inter-cluster versus intra-cluster ferromagnetic alignment.¹²⁶ The intra-cluster ferromagnetism is supported by double exchange while the inter-cluster alignment is quite weak. After cooling to low T in zero-field, each cluster will be spontaneously ferromagnetically ordered, but with a magnetization oriented randomly in relation to other clusters. The random orientation of cluster magnetizations will result in a small net sample magnetization. As the temperature is increased, thermal energy will permit the cluster magnetizations to rotate, promoting cluster-to-cluster alignment and thus the net sample magnetization will increase. As the temperature is increased further, however, thermal energy will begin to disrupt the intra-cluster ferromagnetic alignment, leading to a net reduction of the magnetization.¹²⁶ At some intermediate temperature the magnetization will be maximized. This will correspond to the peak in ZFC magnetization. Similar evidence for the existence of a ferromagnetic cluster glass comes from ac susceptibility data where the out-of-phase component χ'' shows a peak at T_c , but also a second, broader, and frequency dependent peak just below T_c .¹²⁶

The ground state for doping $0 \leq x < 0.18$ is a spin glass. The magnetization in the low-doping regime is also shown in Fig. 4.3. In these measurements, while the FC magnetization at $x = 0.18$ is quite Brillouin-like, as the doping is reduced, the FC magnetization becomes progressively less Brillouin-like.¹²⁶ The ZFC magnetization is peaked at a temperature below T_c , with this peak shifting to lower temperatures as doping is decreased. The peak also becomes sharper and more cusp-like with reduced doping, taking on the characteristic of the cusp seen in measurements of spin glasses. For this reason, this peak has been attributed to a spin-glass freezing temperature (T_f).^{126,130}

Resistivity (ρ) versus temperature (R-T)[†] measurements indicate that LSCO is metallic in the C-FM phase and semiconducting or insulating in the SG phase.^{126,130} Example R-T measurements are shown in the left column of Fig. 4.4. With $x = 0.6$, the slope of the R-T curve ($d\rho/dT$) is positive at all temperatures and particularly at low temperature and the residual resistivity is finite. Both of these characteristics are commonly associated with metals. As the doping is reduced to $x = 0.30$, $d\rho/dT$, although positive at high temperatures, becomes negative at temperatures less than about 150 K. However, its residual resistivity remains finite, and $x = 0.3$ LSCO is classified as having metal-like characteristics. At doping levels $x \leq 0.18$, $d\rho/dT$ is negative at all temperatures, while the residual resistivity diverges progressively more as the doping level is reduced. These two features taken together indicate that for doping levels $x \leq 0.18$ LSCO is an insulator. This metal-insulator transition (MIT) is indicated in Fig. 4.2 by a dashed vertical line. These resistivity measurements also define the critical doping level (x_c) as $x = 0.18$.

[†]Resistivity versus temperature measurements will be denoted as R-T, even though the resistivity will be denoted by the commonly used symbol for resistivity, ρ .

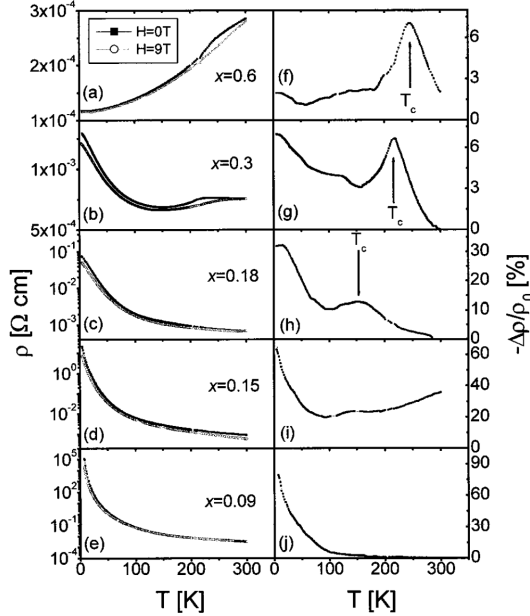


Figure 4.4: Resistivity in 0 T and 9 T (left column) and corresponding magnetoresistance (right column) versus temperature for bulk $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ at various doping levels. Taken from Ref. 126

In the C-FM regime ($x > 0.18$) there is a peak or kink in the R-T curves just below T_c .^{126,130,131} In this regime, the density of FM clusters is such that they form percolation pathways, so that the properties of these hole-rich clusters dominate transport. The peak corresponds to the transition from a negatively sloped ($d\rho/dT < 0$)—insulating-paramagnetic state above T_c to a positively sloped ($d\rho/dT > 0$)—metallic-ferromagnetic state below. That this transition occurs close to T_c suggests that ferromagnetism and metallicity are linked. In the C-FM phase, double exchange between Co^{3+} and Co^{4+} ions within the hole-rich clusters not only promotes alignment of localized spins and therefore ferromagnetism, but also promotes electron delocalization and conduction.¹³¹ When the doping is below x_c , the density of FM clusters is insufficient to form percolation pathways and, although the clusters themselves may be conductive, the insulating intercluster matrix will dominate transport. Thus $d\rho/dT < 0$ at all T if $x < x_c$.

Bulk LSCO has a temperature- and doping-dependent negative magnetoresistance (MR) of as large as 100% for some doping levels. Example MR-T measurements are shown in the right column of Fig. 4.4. The MR temperature dependence has a different character for doping above and below x_c . For doping significantly above x_c (see $x = 0.6$ MR curve in Fig. 4.4), the MR is peaked at about T_c with a values between

6-12%,^{126,130} and then declines at $T \rightarrow 0$ K. The peak in MR has been attributed to a manganite-like CMR.¹²⁶ In this model, LSCO is paramagnetic and insulating above T_c , but ferromagnetic and metallic below. Applying a magnetic field promotes ferromagnetic ordering and LSCO becomes metallic at a higher T . This gives rise to a difference in conductance that is maximized close to T_c . As the doping is reduced ($x \leq 0.3$), the MR begins to increase at all T , but especially at $T \sim 0$ K where a new peak appears. This low- T peak is associated with inter-cluster giant magnetoresistance (GMR).¹²⁶ At this lower doping, the cluster density is too low to produce percolation pathways and conduction is mediated by spin-dependent cluster-to-cluster transport. Applying a magnetic field will promote cluster-to-cluster magnetization alignment and thereby promote transport. As doping is reduced towards x_c , the peak in MR at T_c becomes less pronounced, finally disappearing for doping significantly below x_c ($x = 0.09$). At the lowest doping levels the maximum MR at $T \rightarrow 0$ K approaches $\sim 100\%$.^{126,130}

Further evidence for MEPS in the regime $x < 0.2$ comes from nuclear magnetic resonance (NMR), small angle neutron scattering (SANS), and inelastic neutron scattering (INS). NMR measurements indicate the presence of both a spontaneous ferromagnetism phase and a hole-poor phase at all doping levels $0.1 \leq x \leq 0.4$ in bulk LSCO.¹³² SANS measurements show that, although long-range FM order is no longer detectable for $x \leq 0.15$, FM clusters of x -dependent size between 0.6-2.6 nm remain.¹³³ While INS measurements indicate the presence of FM-order at doping above and below x_c , the magnetic correlation length decreases sharply from ~ 120 Å at $x = 0.2$ down to ~ 5 Å at $x = 0.1$.¹³⁴

What underlies electronic phase separation in cobaltites remains unresolved. One possible cause would be chemical inhomogeneities, with Sr-rich and La-rich regions corresponding to hole-rich and hole-poor regions. High resolution transmission electron microscopy (HREM) measurements of bulk LSCO show regions of 8 to 40 nm in extent where stacking of Sr-rich and La-rich planes appear to occur.¹³⁵⁻¹³⁷ The lack of superstructure spots in electron diffraction measurements does not support the presence of such inhomogeneities.^{136,137} Neutron diffraction measurements also did not show any evidence of chemical inhomogeneities, although Sr-rich clusters of 1.0 to 2.0 nm could not be ruled out.¹³⁶ Finally, statistical simulations indicate that a random distributions of dopants will form 0.6 to 2.5 nm clusters with local doping at or above the threshold for ferromagnetism in bulk, even when the overall doping is below that threshold. These clusters were even found to have the a size distribution consistent with the magnetic correlation length measured with SANS.¹³³

4.2 Films

The properties of films can be different from the bulk due to a variety of factors. These include defects, especially oxygen deficiencies; substrate-induced strain; and the finite-size effect.^{138,139}

The effect of oxygen vacancies is to disable Co-O-Co double exchange, the mech-

anism underlying the ferromagnetic and metallic properties of cobaltites. Such vacancies produce fewer carriers (reduced effective hole-doping) and fewer O-mediated double exchange interactions (reduced exchange energy) resulting in a reduced T_c and a reduced low-T magnetization. The number of oxygen vacancies (the oxygen stoichiometry), however, is largely controlled by the process conditions.^{123,139} Lower growth pressures will produce films with reduced T_c and saturation magnetization (M_s) or even no measurable ferromagnetic properties at all.¹²³ Even after the film is grown, it must be handled with some care. Reducing the oxygen partial pressure during post-growth cool can reduce the oxygen from stoichiometry from 3 down to 2.79.¹⁴⁰ In a similar manner, heating the film in an oxygen poor environment or vacuum can also reduce the oxygen content and even render a nominally metallic LSCO film insulating.¹⁴¹

For epitaxially grown films, any mismatch of lattice parameter between the substrate and film will be taken up by increasing or decreasing the Co-O bond length or by changing the Co-O-Co bond angle. Any change in bond length or bond angle can cause either an increase or decrease in transfer function bandwidth. For example, 1.5 % in-plane tensile strain (22 nm LSCO film on SrTiO_3) will reduce T_c by ~ 15 %, while 0.7 % in-plane compressive strain (22 nm LSCO film on LaAlO_3) will increase T_c by ~ 5 %.¹³⁹

Another factor relevant to films but not to bulk LSCO is the finite-size effect which was shown to play a role in reducing T_c and M_s on thinner LSCO films.^{138,139} It comes into play whenever a ferromagnetic film is thinner than the spin-spin correlation length.^{138,139} So, for example, on a 22 nm thick LSCO film the T_c is reduced by about 20 K from that of a bulk sample by the finite-size effect alone.¹³⁹

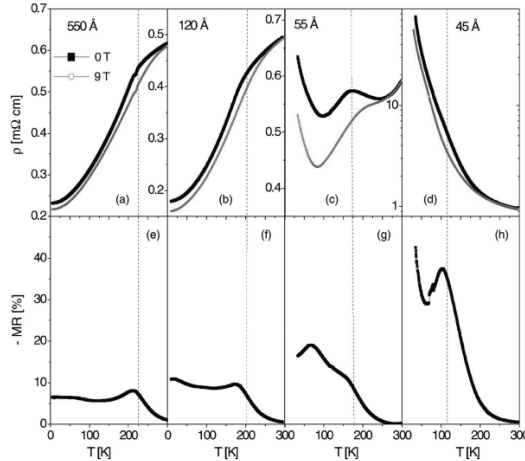


Figure 4.5: Resistivity in 0 and 9 T magnetic fields (top row) and magnetoresistance calculated from this data (bottom row) for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ films of thicknesses 4.5 through 55 nm. Taken from Ref. 123

Of interest for this investigation is evidence from magnetic and transport measurements which indicate that very thin ($t < t^*$) $x = 0.5$ LSCO films grown on SrTiO_3 are also phase separated. This evidence comes from the close similarity between magnetic and transport measurements of films $t < t^*$ with measurements of $x \leq 0.18$ doped bulk samples.^{123,124} Much like low-doped bulk samples, films thinner than t^* have a reduced M_s ; a large-magnitude, hysteretic MR; and are insulating ($d\rho/dT > 0$). Field-dependent magnetoresistance measured on 5.5 nm thick $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ films^{123,124} (not shown) are alike measurements of phase-separated bulk LSCO, while thicker films have field-dependent magnetoresistance of much smaller magnitude with characteristic AMR behavior. Whereas films thicker than t^* [Fig. 4.5(a), (b)] are metallic similar to $x = 0.6$ doped bulk [Fig. 4.4(a)], thinner films [Fig. 4.5(d)] are insulating similar $x \leq 0.18$ bulk [Fig. 4.4(c)-(e)]. These similarities do suggest that very thin LSCO films are phase separated just as low-doped, $x \leq 0.18$, bulk LSCO is.

4.3 Film growth and characterization

Two $x = 0.5$ LSCO films were deposited onto $\text{SrTiO}_3(001)$ substrates by high-pressure reactive dc magnetron sputtering in an O_2 and Ar mixture with a $\text{P}_{\text{O}_2}/\text{P}_{\text{Ar}}$ ratio of 0.4 and total pressure 140 mTorr. During growth the substrates were held at approximately 700 °C. Following growth, the films were cooled in 500 Torr of O_2 and then post-growth annealed at 500 °C in flowing O_2 to remove any CoO impurity phase. The film thicknesses were measured with grazing-incidence X-ray reflectometry using Cu $K \alpha$ radiation. Further details of the growth and characterization of these films can be found in Ref. 123.

Conductance maps and STS measurements were made under ultra high vacuum (UHV) conditions using an STM head built in-house. The UHV STM chamber has a base pressure of 4×10^{-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. Mechanically cut PtIr (90%:10%) STM tips were used exclusively. Conductance maps and STS were made in the same way as detailed earlier (see Section 3.2.2). It is worth reiterating here that all of the conductances shown in this Chapter were measured by lock-in at the tunneling set-point (and actually should be called differential conductance). This means that a shift to higher (lower) conductance equates to a more insulating (metallic) IV . This can be seen by comparing the set-point slope of the two IV 's shown in Fig. 4.9(c). The more metallic curve (heavy line) is shallower than the more insulating curve (fine line) and so has a lower set-point conductance. Since this can easily lead to confusion, the terms 'more metallic' or 'more insulating' will also be used regularly

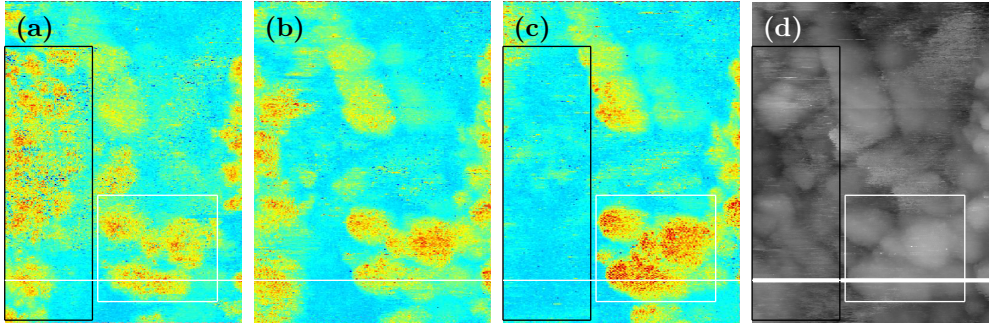


Figure 4.6: Conductance map of 4.7 nm film measured in magnetic field. Dark red areas are more metallic, dark blue areas more insulating. (a) 0 T, (b) 4 T, (c) 8 T, and (d) topography of same area of film (measured at 3.7 K, setpoint 0.70 V and 210 pA, scan size 55 nm $\times$ 74 nm). Horizontal lines indicate position of sections shown in Fig. 4.7. Black and white boxes explained in text.

4.4 Results

The evidence from the literature presented so far suggests that very thin $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ films should be electronically inhomogeneous while thicker films should be homogeneous. In the following section we examine evidence from STM measurements of two $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ films, one thinner ($t = 4.7$ nm) than t^* and the other thicker ($t = 12.4$ nm). These measurements include conductance maps and IV spectroscopy. Both the conductance maps and spectroscopy indicate that the thinner LSCO film is inhomogeneous while the thicker LSCO film is largely homogeneous.

4.4.1 Thinner Film ($t < t^*$)

Conductance maps of the 4.7 nm were consistently inhomogeneous. Two examples of conductance maps from this film are shown in Figs. 4.6 and 4.8. In these maps the darker red areas are more metallic while the darker blue (Fig. 4.6) or lighter orange (Fig. 4.8) areas are more insulating.[†] Both areas of the film shown in these conductance maps appear inhomogeneous, composed of metallic areas embedded in an insulating matrix. Qualitatively speaking, they are inhomogeneous in the sense that they are made up of large, contiguous areas of similar color or, equivalently, conductance. All other conductance maps (not shown) measured on this film were inhomogeneous. Figs. 4.6 has a hierarchy of metallic clusters, with 5 - 30 nm size grains forming clusters of 30 - 60 nm size. On Fig. 4.8 there are both smaller, 5 - 10 nm grains (lower left), and larger, 30 - 40 nm grains (top). Other areas of the film (not shown) were similar to these two Figures. In some places on the film, the grains

[†]This assignment of metallic and insulating was verified with IV spectroscopy. See discussion that follows regarding Fig. 4.8(c) and Fig. 4.9(c).

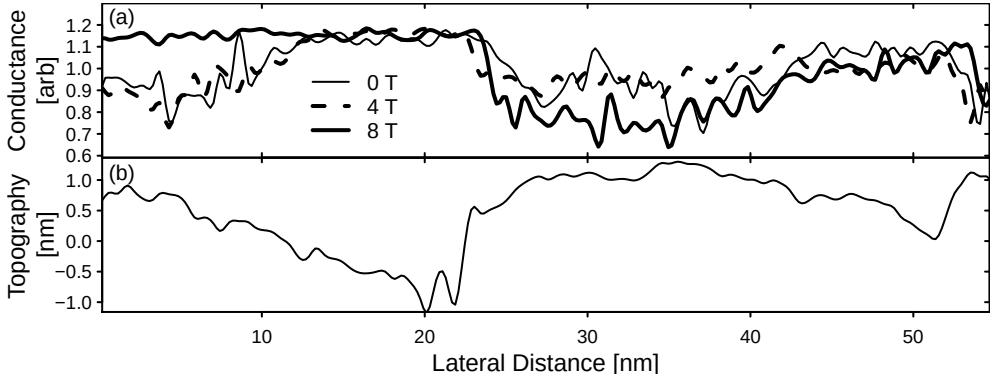


Figure 4.7: Section through conductance and topography from Fig. 4.6. Note that a higher (differential) conductance value signifies a more insulating area.

are far less apparent, and the metallic regions extended to 100 nm or larger.

In some areas of the inhomogeneous film the conductance is correlated with topography. One area of particularly strong correlation is indicated by the white box in Fig. 4.6(a). Comparing this area of the conductance map to the corresponding topography [white box in panel (d)], a correspondence between topography and conductance is clear, with dark grains on the conductance map aligning closely with grains in the topography.[†]

This correspondence can also be seen in sections through the conductance maps and topography. Example sections are shown in Fig. 4.7. The location of these sections is indicated by horizontal white lines in Fig. 4.6. In particular, the decrease in zero-field conductance (fine line) that occurs at the same location (lateral distance ~ 22 nm) as the increase in topography. In fact, between about 26 and 50 nm lateral distance, the conductance and topographic sections are almost the inverse of each other.

In other areas of the inhomogeneous film there is only a weak correspondence between conductance and topography. Compare the black box in Fig. 4.6(a) to the black box in (d). While some features in the conductance map, (a), do correspond to features in topographic map, (d), the apparent grains in the conductance maps are smaller than those in the topographic map. Similarly, the conductance and topography shown in Fig. 4.8(a) and (d), respectively, are only weakly correlated.

The effect of magnetic field on the conductance of the inhomogeneous film is mixed, with no obvious trend in behavior. While some areas of the film become darker or lighter in an applied field, other areas appear unchanged. Examples of in-field conductance map are shown in Figs. 4.6 and 4.8. Fig. 4.6(a), (b), and (c) show a sequence of conductance maps measured on the same area of the film but in 0, 4, and 8 T applied magnetic fields, respectively. Fig. 4.8(a), (b), and (c) show a sequence of conductance maps measured in 0, 4, and 6 T applied magnetic fields, respectively.

[†]The correlation is most apparent in the conductance map measured at 8 T shown in panel (c).

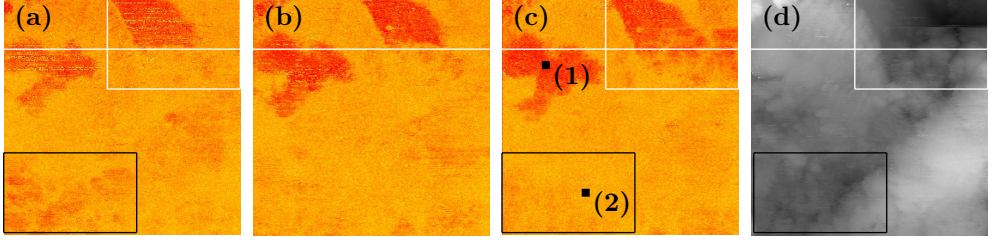


Figure 4.8: Conductance map of 4.7 nm film measured in magnetic field. (a) 0 T, (b) 4 T, (c) 6 T, and (d) topography of same area of film (measured at 7.5 K, setpoint 1.0 V and 408 pA, scan size 90 nm $\times$ 90 nm). Dark red areas are more metallic, light orange areas more insulating. Horizontal lines indicate position of sections shown in Fig. 4.9. (1) and (2) indicate position where *IV* curves (shown in Fig. 4.9) were measured. Black and white boxes explained in text.

One area of the film that becomes more metallic in field is shown in Fig. 4.6, highlighted by a white box. In an 8 T field [panel (c)], the metallic grains within this area are darker and larger than they were in zero field [panel (a)]. This can also be seen in the conductance section in Fig. 4.7(a). Compare the 0 T section (fine line) to the 8 T section (thick line). Between lateral distance 25 and 35 nm, the 8 T conductance is approximately 10 % below the 0 T conductance.

Another area of the film that becomes more metallic in field is shown within the white boxes of Fig. 4.8(a)-(c). In this case there is already a significant metallic region present at 0 T. However, this region increases substantially in size in a 6 T applied field. The same is true of the dark region to the left of the white box. Again this is corroborated by the sections through these conductance maps shown in Fig. 4.8(a). In particular, between lateral distance 0 to 20 nm and 50 to 90 nm, the 6 T section (heavy line) is significantly below the 0 T section (fine line), indicating that this area of the film has become more metallic.

Some areas of the film, however, become more insulating in an applied magnetic field. One example is the area highlighted by the black box in Fig. 4.6. The dark red area visible at 0 T inside the black box in (a) is largely gone once an 8 T field has been applied. This is also apparent in the conductance sections shown in Fig. 4.7(a). Compare the 0 T conductance (fine line) and the 8 T conductance (heavy line). Between lateral distance 0 and 15 nm, the conductance has increased by as much as 20% at 8 T compared to 0 T. Another part of the inhomogeneous film that becomes lighter in field is the area indicated by the black box in Fig. 4.8. At 0 T, the conductance in this area [panel (a)] is substantially redder than the same area measured in a 6 T applied field [panel (c)].

No trend towards metallic or insulating is apparent. To illustrate this, a histogram of the conductance in Fig. 4.6 at 0, 4, and 8 T shown in Fig. 4.10(a). In this case the effect of an applied field is to shift the overall conductance from low values to high values, increasing the height of the peak at conductance ~ 4.8 and reducing the

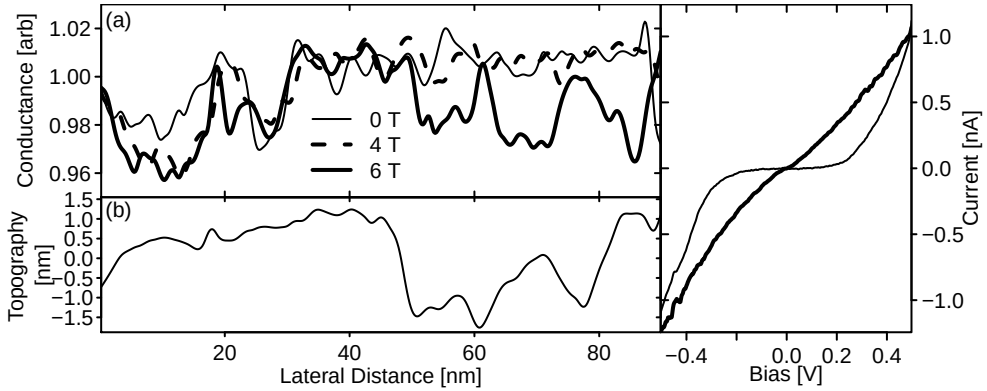


Figure 4.9: Section through (a) conductance and (b) topography maps shown in Fig. 4.8 and (c) IV curves measured on the same film (7.5 k, setpoint 0.5 V and 1 nA). Heavy and fine lines in panel (c) correspond to locations (1) and (2) in Fig. 4.8. Note that a higher (differential) conductance value signifies a more insulating area.

shoulder between conductance 2.5 and 4.5. A shift like this to higher conductance values corresponds to an increase in the proportion of conductance map that is insulating. Certainly this is consistent with the overall shift from dark red/yellow to blue apparent in Fig. 4.6(a), (b), and (c), and particularly so in the area within the black box. Conductance histograms from other areas of the film, however, were largely unaffected by an applied field. One example of such an area is that shown in conductance map histogram shown in Fig. 4.10(b). This histogram was taken from the conductance maps of Fig. 4.8(a)-(c). On this area of the film, an applied field shifts the peak at ~ 5.45 to a slightly higher conductance—as with the example in panel (a). However, the low-conductance shoulder increases slightly between conductances 5.2 and 5.3—unlike the histogram in panel (a). Although this behavior is not the same as seen in the panel (a) histogram, it is consistent with the appearance of the conductance map in Fig. 4.8 which does not have an overall shift towards lighter or darker in field.

Evidence from STM point spectroscopy also indicate that the thinner film is inhomogeneous. Examples of spectroscopy are shown in Fig. 4.9(c). These spectra were measured in the area of the film shown in Fig. 4.8, at locations labeled (1) (red area, heavy line) and (2) (orange area, thin line). The zero bias conductance (ZBC) of these two IV 's illustrates the significant difference in electronic properties of the thinner film. The ZBC of the IV measured on the darker area is 1.6 nA/V, while the ZBC of the IV measured on the lighter area is 1.4×10^{-2} nA/V. The ZBC on the darker area is, thus, ~ 120 times larger than the ZBC on the lighter area. Other spectra measured on other areas of the film were consistent with this. That is, IV spectra measured on dark areas are more metallic while IV spectra on light areas are more insulating.

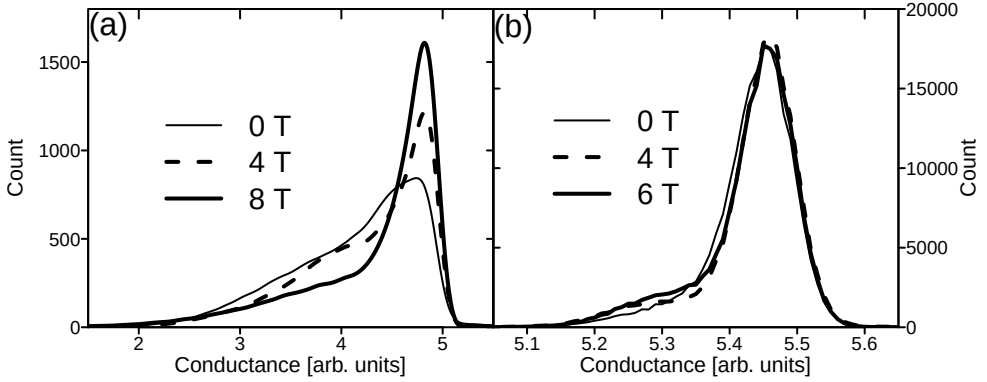


Figure 4.10: (a) Histogram of conductance from Fig. 4.6(a)-(c). (b) Histogram of conductance from Fig. 4.8(a)-(c). Note that a higher (differential) conductance value signifies a more insulating area. See text for further detail.

Taken together, the conductance maps and spectroscopy indicate that 4.7 nm film is electronically inhomogeneous. While this is unambiguous, the effect of a magnetic field on the conductance has no clear trend. What these in-field measurements do show is that these inhomogeneities are not-magnetically inert chemical inhomogeneities or structural artifacts (defects or varying crystallography). That, though, does not rule out these effects as playing a role in the electronic inhomogeneity.

4.4.2 Thicker Film ($t > t^*$)

Evidence from conductance maps and IV spectroscopy indicate that the 12.4 nm film is substantially more homogeneous than the 4.7 nm film. An example conductance map shown in Fig. 4.11(a) with corresponding topography in panel (b). This conductance map appears homogeneous, with no contiguous areas of similar conductance (tone). There is also no evidence of a correlation between conductance and topography.

Section through conductance map and topography shown in Fig. 4.12, panels (a) and (b), respectively. The position of these sections is indicated in Fig. 4.11 by a white horizontal line. The conductance map section is featureless and does not correlate to the topography section. There are no abrupt changes in conductance where there are abrupt changes in topography. While, for instance, the topography drops a total of 7 nm between lateral distance ~ 8 nm and ~ 170 nm, no such pattern is seen in the conductance.

STS also indicates that the thicker film is largely electronically homogeneous, although not as homogeneous as the conductance map would suggest. Example IV spectra from this film are shown in Fig. 4.12(c). These spectra are taken from set of 16 measured along the diagonal of a $300 \text{ nm} \times 300 \text{ nm}$ area. These measurements

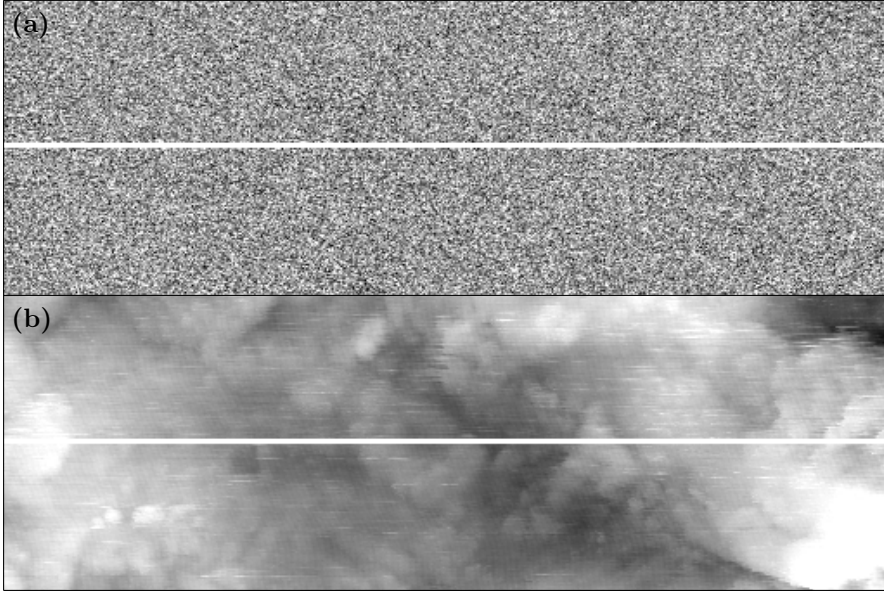


Figure 4.11: (a) Conductance map and (b) topography of 12.4 nm film in zero magnetic field (measured at 1.7 K, setpoint 0.6 V and 219 pA, 300 nm $\times$ 100 nm). White lines indicate location of sections shown in Fig. 4.12.

were made in the same area of the film shown in Fig. 4.11. Of these 16 *IV*'s, 15 were very similar to the finer line *IV* shown in the Figure, so for clarity only one is shown. The zero bias conductance (ZBC) of these 15 *IV*'s is very similar with a mean of 1.4×10^{-2} nA/V and standard deviation of 8.4×10^{-3} nA/V. The remaining *IV* is plotted with a heavier line in the Figure. The ZBC of this *IV* is 3.9×10^{-1} nA/V, about 30 times larger than the ZBC of any of the other 15 *IV*'s. Other sets of *IV*'s taken at other set-points and at different locations were similarly homogeneous, i.e. largely similar *IV*'s with at most one outlier. These outliers suggest that although the film was largely homogeneous, there are small areas or hotspots with higher conductance.

4.4.3 Comparison of 4.7 nm Film and 12.4 nm Film

A comparison of conductance maps and point spectroscopy measured on the thinner film versus the thicker film, indicates that the thinner film has characteristics which at first sight are consistent with magneto-electronic phase separation (MEPS), while the thicker film does not.

To aid in further comparison of the electronic properties of the 12.4 nm and 4.7 nm films, sections through conductance maps of both films are collected in Fig. 4.13. Shown in panel (a) is a section of the 4.7 nm film taken from Fig. 4.6(a). Shown in panel (b) is also a section from the 4.7 nm film, but taken from Fig. 4.8(a). Finally,

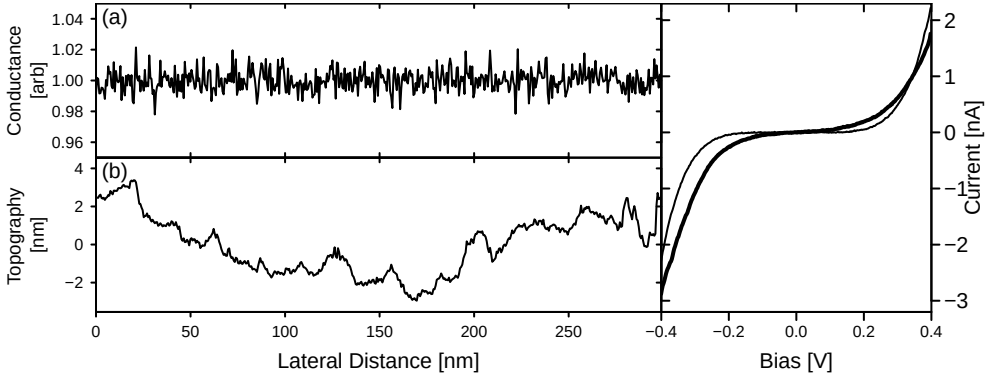


Figure 4.12: Section through (a) conductance and (b) topography maps shown in Fig. 4.11 and (c) IV curves measured on the same film (1.7 K, setpoint 0.35 V and 1 nA). See text for further detail.

shown in panel (c) is a section through the 12.4 nm film taken from Fig. 4.11(a).[†] The conductance sections through the thinner film appear to deviate for longer from the mean value than the section through the thicker film. While the deviation from the mean is most obvious in the section shown in panel (a), it is still apparent in the section shown in panel (b). This can be made more quantitative by calculating autocorrelation functions of these sections to test for randomness. These calculations reveal that the autocorrelation coefficients of the sections through the thinner film remain statistically different from zero (95% confidence level) up to a lag of ~ 30 (30 pixels or 5.9 nm). The correlation maps from the thinner film therefore have spatial structure with features of size up to ~ 5.9 nm. On the thicker film, the autocorrelation coefficient of lag 1 (1 pixel or ~ 0.6 nm) is already below the 95% confidence band and remains so for all calculated lags. As such the autocorrelation coefficients of the thicker film are statistically indistinguishable from zero. The correlation map for the thicker film is therefore uncorrelated noise at the scale of ~ 0.6 nm or larger. This corresponds closely to the qualitative picture from both the conductance maps and conductance map sections.

4.5 Discussion

The above STM measurements provide evidence of the existence of a critical thickness in the $\text{LSCO}(x = 0.5)/\text{STO}$ system, separating films with different properties. From

[†]For clarity, the scale of panel (a) of Fig. 4.13 is different from the scale in panels (b) and (c). This was done to compensate for the difference in relative variation of the normalized conductance. Part of this variation stems from the tunneling barrier and part is from variations in sample electronic properties. Separating the influence of these two factors is difficult due to the highly non-linear nature of tunneling, making an comparison of absolute conductance variations difficult.

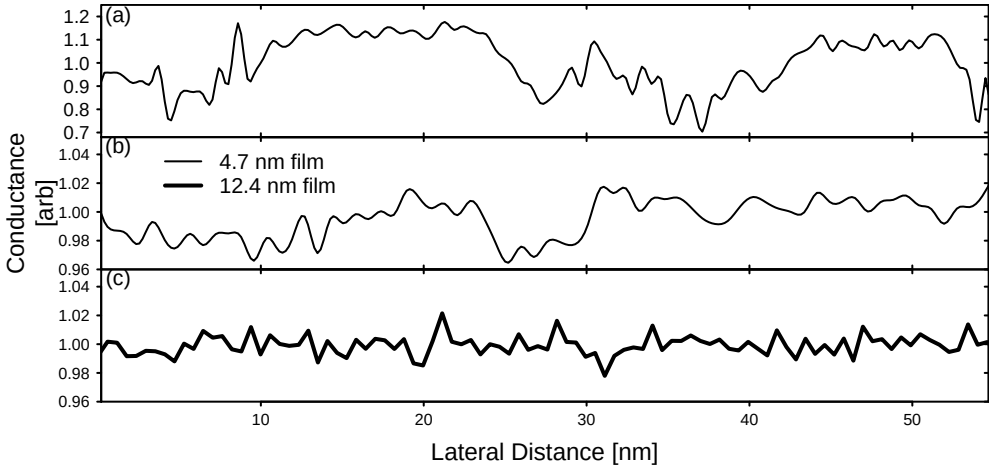


Figure 4.13: Comparison of sections through conductance maps. (a) Section of 4.7 nm film from Fig. 4.6(a). (b) Section of 4.7 nm film from Fig. 4.8(a). (c) Section of 12.4 nm film from Fig. 4.12(a).

both conductance maps and point spectroscopy it follows that the 4.7 nm ($t < t^*$) LSCO film is electronically inhomogeneous, with metallic regions of size from 5 to more than 100 nm, embedded in a more insulating matrix. They also show that the thicker 12.4 nm film ($t > t^*$) is much more electronically homogeneous than the thinner film, with no contiguous areas of different conductance, but rather random variation on the scale of a pixel. Autocorrelation function analysis of sections through the conductance maps confirms this, showing that the conductance of the thicker film is without features on a scale larger than ~ 0.6 nm, the resolution limit of the data.

The conclusion from magnetism and transport measurements was that the observed low-thickness enhanced resistivity is intrinsic, in the sense that the decrease in conductivity above t^* is not simply due to the non-coalescence of isolated metallic islands which are present at all thicknesses. The data pointed to either a homogeneous ferromagnetic insulator phase for $t < t^*$, or a phase separated material with a non-F phase in between metallic F domains which only occur at low thickness.^{123,124} The STM data unequivocally support the latter picture. The conductance maps of the 4.7 nm film show the presence of metallic grains ranging from 5 to 30 nm that, in some areas of the film, form clusters of 100 nm or larger. This is similar in scale to the ferromagnetic domains measured by SANS on $x = 0.5$ LSCO films ($t = 65$ nm),¹²⁴ and which were thought to reside close to the interface.

The STM data also indicate that the metallic clusters are magnetic, since they are sensitive to an applied magnetic field. The sign of the effect at first sight may be surprising, since the field tends to render metallic areas more insulating. The reason for this may be found in a possible large spread of strongly pinned magnetization directions (which also leads to the low magnetization found in such thin films). If

clusters with different ferromagnetic directions are not rotated simultaneously, inter-cluster tunneling will actually lead to decreased conductance. The sluggish variation of the metallicity in rather high fields, as demonstrated in Fig. 4.10, therefore points to the metal phase consisting of small, almost spinglass-like, ferromagnetic clusters. Then, the data show that the metallic phase does not keep on growing when the film becomes thicker. Instead what is grown is now quite a homogeneous material.

But what exactly is the underlying cause of the phase separated state? Here, one point should be mentioned which was not discussed before, namely that the zero bias conductance of the metallic clusters appears to be significantly larger (two orders of magnitude) than either the insulating phase surrounding them or (and more importantly) the homogeneous phase appearing at higher thickness. This fact strongly indicates a chemical nature of the electronic inhomogeneities.

This agrees very well with electron energy loss spectroscopy measurements on such films, which indicate a lower-than-nominal hole doping close to the interface, due to small variations in the Sr- and O-content.¹²⁴ The nominal doping found within about 10 nm of the interface corresponds to $x = 0.24$, very close to the doping where phase separation occurs in the bulk. In turn, the origin of the compositional variation might be found in strain-driven segregation, and so provide a natural explanation for the existence of a critical thickness. This picture as it emerges from the literature is strongly supported by the real space STM data presented here.

Outlook

The STM measurements presented have hardly exhausted the possible scanning probe microscopy measurements of LSCO. In particular, it would be of interest to compare the present data on LSCO films with $x = 0.5$ and two thicknesses above and below t^* with (i) such films grown on a non-straining substrate and (ii) on films with $x < 0.2$, in the phase separated spinglass regime. In particular, it can be expected that the latter show spatial variations of the conductance not unlike what has been found here for the 4.7 nm film. Films doped $x = 0.22$ and $x = 0.28$ have critical thicknesses, 30.0 nm and 15.0 nm, respectively.¹²⁴ Measurements of LSCO films with these doping levels would provide a way to examine whether the STM results presented above are generally applicable, or specific to LSCO films doped $x = 0.5$.

With respect to the substrate-induced strain, the films measured here were exclusively grown on SrTiO_3 . This substrate imposes a biaxial tensile strain of about 1.5% on $x = 0.5$ doped LSCO. Films could also be grown on other substrates. For example, the effect of compressive strain of about -0.7% could be studied by growing a LSCO film on LaAlO_3 . Unfortunately, as no substrates are available with the same lattice constant as LSCO, unstrained LSCO films cannot be studied directly.¹³⁹ Nevertheless, comparing films under compressive versus tensile strain may provide insight into the formation of MEPS in LSCO films.

Chapter 5

Ferromagnet/Superconductor Bilayers

In this Chapter, scanning tunneling spectroscopy (STS) measurements on weak ferromagnet/superconductor bilayers are discussed. The focus will be on the occurrence of the so-called zero-bias conductance peak (ZBCP) in a hybrid ferromagnet/superconductor (FS) system. The ZBCP is a general feature of the tunneling spectrum which is found in the gap under various circumstances, signaling the presence of a finite density of states at zero energy. As will be shown, performing spectroscopy by STM is of particular interest, since the anomaly can be more pronounced than in the case of lithographically prepared junctions, which often suffer from averaging effects. Moreover, more information on the mechanisms behind the ZBCP can be gained from the spatial variation measured by STS. The first section will be a general introduction in the ZBCP phenomenon, followed by a set of measurements on the bilayer system Nb/Cu₄₁Ni₅₉.

5.1 Introduction

5.1.1 Andreev Reflections

The ZBCP is a general phenomenon, which has been observed on high- T_c superconductors, in the core of superconducting vortices, and on the F-side of an FS bilayer. It is easiest introduced through a brief discussion of the proximity effect between a superconductor and a normal (N) metal. The proximity effect is the process by which Cooper pairs can leak from the S metal into the N metal. The characteristic length over which the superfluid density or the superconductor order parameter decays is given by the coherence length ξ_N , which in the dirty limit (meaning the mean free path l is smaller than the coherence length) is given by $\xi_N = \sqrt{(\hbar D_N)/(2\pi k_B T)}$, where D_N is the electron diffusion constant in the N metal. In a similar fashion, on the S-side of the junction the superconducting density is depleted over a length which is set by the superconducting coherence length, given by $\xi_S = \sqrt{(\hbar D_S)/(2\pi k_B T_c)}$. Note that ξ_N can become very large when $T \rightarrow 0$. The mechanism by which Cooper

pairs leak across the interface from the S to the N-metal is via Andreev reflection (AR). This process is illustrated in Fig. 5.1. It shows the probabilities for pair occupation (in S) or electrons (in N) versus wave vector at $T = 0$. There are Cooper above the Fermi wave vector k_F up to roughly $k_F + \Delta/(\hbar v_F)$ but there are no single-electron states available in the range $k_F \pm \Delta/(\hbar v_F)$. There are two mechanism by which pairs can be transported into the normal metal. One is by Cooper-pair breaking at an energy cost of $E = 2\Delta$ and the other is via Andreev reflection for $E < \Delta$. At $T = 0$ Andreev reflection is the only option. In the Andreev reflection process, a spin-up electron (e) with E_e larger than the Fermi energy (E_F) is injected into the conduction band of the N metal, while a spin-down hole (h) with $E_h < E_F$ is injected from the N-metal valence band into the S.[†] In effect two electrons (with zero net spin) have been removed from the condensate. Since $E_e > E_F$, the electron will have a wave vector, $k_e = k_F + dk$, while the hole, with $E_h < E_F$, will have wave vector $k_h - dk$, where $dk = E/\Delta v_F$. This means that, except when $E_e = E_h = E_F$ and, thus, $dk = 0$, the Andreev pair will have a non-zero center of mass momentum and a wave vector of $2dk$. This means that as the pair travels into the N metal it accumulates a net phase shift of $2dkz$, where z is the distance traveled perpendicular to the NS interface. The electron-hole correlation therefore gradually disappears, which is the basis for the proximity length in N.

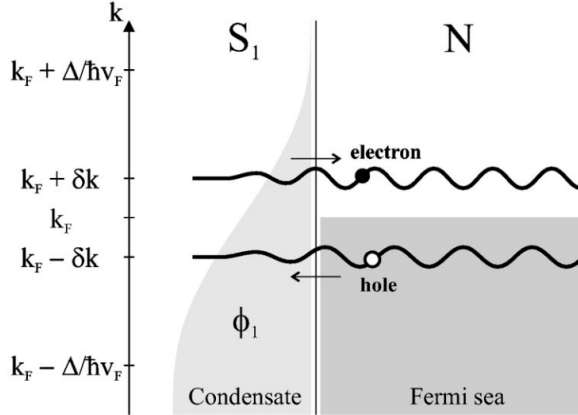


Figure 5.1: Illustration of Andreev reflection at normal metal-superconductor interface. Taken from Ref. 142

The NS proximity effect lends itself to investigation via tunneling experiments and have been performed both with planar junctions and STS. Planar junctions are constructed as a C/I/N/S configuration (C a metal contact, I an insulating layer). The tunneling occurs between the C and N layers and the excitation spectrum of the Andreev pairs proximized into the N-metal side of the NS bilayer is measured. Except

[†]The process works equally well with a spin-down electron and spin-up hole

where noted, this is the configuration of tunnel junctions discussed here. The signature of Andreev pairs on the N-metal side of the junction is a gap in the differential conductance, that is related to the original superconducting gap Δ , but also depends on the distance from the interface z . The gap is smaller than the original (a minigap) and narrows with increasing z . At zero energy (zero bias) the DOS is zero, except when there are pair breaking effects in the N layer. In that case the gap is a pseudogap. With STS, this behavior has for instance been probed using Au islands on NbSe2 crystals.^{143–145} Also, Moussy *et al* measured 1.5 μm diameter Nb dots with a 20 nm Au layer that covered both the dots and the bare substrate.¹⁴⁶ In this configuration, the Au will be proximized upward from the Nb dot in a direction perpendicular the Au film plane and horizontally away from the Nb dot within Au-film plane. On top of the Nb dots the Au film is thin and they observed tunneling spectrum with minigaps. Away from the Nb dots the proximity effect works within the plane of the Au film and Nb, therefore, is effectively very long. Here they observed pseudogapped tunneling spectra.

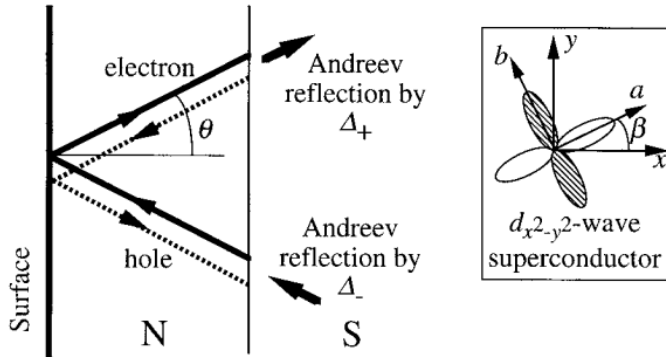


Figure 5.2: Formation of bound states in an NS bilayer where the phase of the order parameter, indicated by $\Delta_{\pm}$ of the superconductor is different for different k -vectors. The right-hand picture shows the lobes of a d -wave superconductor, which carry different phases. Taken from Ref. 147.

A slightly different way to consider the density of states at the N surface of an NS bilayer is to realize that the combination of a finite pair potential in the S layer with a zero pair potential plus a reflecting surface in the N layer actually form a potential well which can set up Andreev bound states. It was already discussed by de Gennes and Saint-James that for the NS case such bound states occur at a finite energy below Δ , approaching Δ when d_N becomes small. This changes when, during the round trip of the electron in the well, somehow an extra phase is picked up. If this phase equals π , bound states at zero energy occur, which are at the basis of the ZBCP. There are several well-known cases which lead to such bound states. One is found in the realm of high- T_c superconductors. Shown in Fig. 5.2 is the

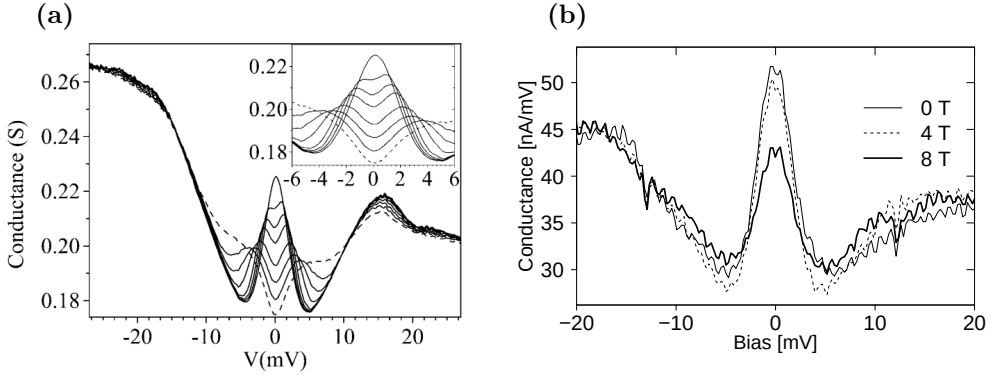


Figure 5.3: (a) Conductance of YBCO measured with planar junction in magnetic fields 0, 0.2, 0.3, 0.4, 0.6, 1, 2, and 4 T (dashed line). Taken from Ref. 148. (b) Conductance from STM measured in field at ~ 4 K.

situation of an NS bilayer, in which the S layer has an order parameter with different phases for different incoming directions or k -vectors of the electron. The extra phase difference picked up in the reflections of electron and hole will now in general lead to a bound state at zero energy, and therefore a density-of-states feature at zero bias. It was subsequently shown that such a bound state even occurs when $d_N \rightarrow 0$, at the surface of a high- T_c material. Looking more closely at the lobes of the d-wave order parameter shown in Fig. 5.2, there will be a difference for different crystalline directions. Without going into details, tunneling along the c-axis direction of a material such as $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO), orthogonal to the lobes which are located in the a-b planes of the material, will not show a bound state. Tunneling along the a-b planes in a $[110]$ -direction, however, will show the ZBCP. Here the difference between planar junction and STM/STS can be very nicely demonstrated.

Figure 5.3(a) shows a conductance measurement at 4.2 K on a planar junction made of indium and YBCO, fabricated in such a way that the tunneling direction is $[110]$. The ZBCP is clearly visible, with a relative height (peak maximum divided by baseline) of about 25 %. Fig. 5.3 shows an STS spectrum measured with the Leiden UHV-STM at ~ 4 K, on a $[110]$ -oriented YBCO. Here the relative height of the peak is greater, attributable to the absence of smearing effects that take place in a large junction. In field, the planar junction ZBCP decreases and then splits, while the STS ZBCP decreases but does not split. This difference is likely caused by the orientation of the field in these two examples: in the planar junction experiment, the field is oriented along the c-axis (perpendicular to the ab-plane), while in the STS experiment, because of the position of the sample within the STM, the field is oriented along the $[110]$ -direction (within the ab-plane). The orientation of the field is quite critical for observing a ZBCP split. This has been demonstrated in planar junction experiments where applying the field perpendicular to c-axis (still tunneling into the

[110] direction) produced a diminished but un-split ZBCPs.^{149†}

A second example of the occurrence of a zero-bias anomaly is in the core of an Abrikosov vortex. The vortex contains one flux quantum, and the superconducting order parameter has a singularity in the core center, which makes it a type of normal potential well. It was demonstrated by Kashiwaya *et al* that for quasiparticles particles trapped in the core and passing through the center, the sign of the pair potential changes.¹⁴⁷ This extra phase of π then leads to a ZBCP in the core center, as was measured by Hess *et al* on the surface of clean NbSe₂ crystals.¹⁵⁰

The third example of the occurrence of a ZBCP is in the case that the N metal is replaced by a ferromagnet. For certain thicknesses of the F-layer, the order parameter can change its phase and again the AR process leads to bound states at zero energy. This is explained in some more detail in the following Section.

5.1.2 FS Bilayer

The generic difference between an F or an N layer in contact with an S layer can again be best explained in terms of Andreev reflections. Important now is that a Cooper pair is made up of two electrons with different spins, which form a spin singlet. When such a pair diffuses into the ferromagnet, one electron will be oriented parallel to

[†]We attempted to introduce a c -axis field component to our measurements by tilting our [110]-oriented samples by 45° but still saw no splitting.

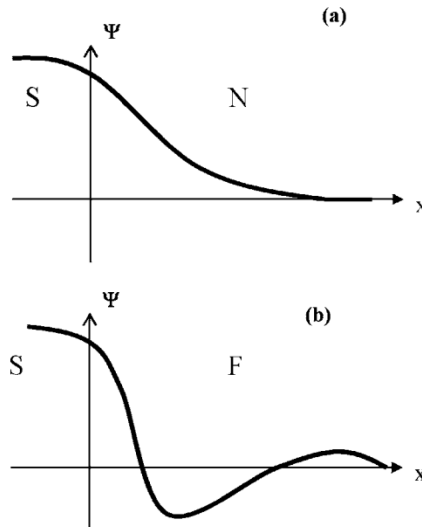


Figure 5.4: Behavior of order parameter in the vicinity of the interface (a) between a superconductor-normal metal and (b) between a superconductor-ferromagnetic metal junction.¹⁵¹

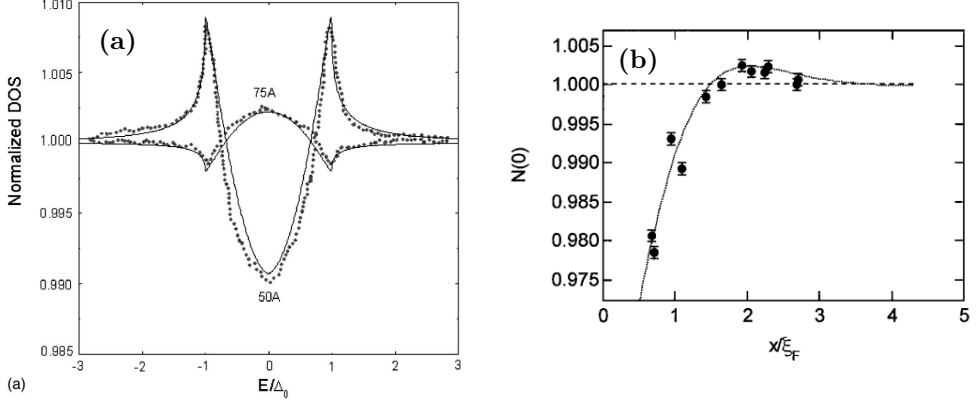


Figure 5.5: (a) Tunneling spectrum measured on $\text{Pd}_{0.9}\text{Ni}_{0.1}/\text{Nb}$ bilayer planar junctions (broken line), and theoretical fit to data. Taken from Ref. 152 The PdNi film thickness is as indicated. (b) Zero bias conductance plotted as a function of normalized PdNi film thickness. Taken from Ref. 153

the magnetization, and the other antiparallel. The potential energy of the parallel (antiparallel) electron will decrease (increase) by an amount equal to the exchange energy (E_{ex}) of the F and energy conservation requires that the parallel (antiparallel) electron increase (decrease) its kinetic energy. This changes the wavevectors to $k = k \pm q$, with $q = E_{ex}/(\hbar v_F)$. The Andreev pair therefore acquires a net momentum of $Q = 2q$. Because of the requirements of fermionic asymmetry, a pair with momentum $-Q$ must also be considered. Superposition of these two pairs results in a singlet combination, producing an oscillation in the order parameter or, equivalently, a pair amplitude of $F \propto \cos(2qz)$. The difference between the order parameter behavior in N and F is sketched in Fig. 5.4.

The characteristic decay length ξ_1 and the characteristic oscillation wavelength ξ_2 of the order parameter are the same in the dirty limit and, without considering spin-flip processes, is given by $\xi_{1,2} = \sqrt{(\hbar D_F)/E_{ex}}$, where D_F is the diffusion length in F. Of importance is that a node in the order parameter appears for a thickness of the F-layer larger than roughly ξ_2 , which means that a phase change of π will occur. In the π state, a ZBCP will be found at the surface of the F layer. Because of the exponential decay of the pair potential, it will only be detectable for relatively small d_F . To have better control over such samples, it is advantageous to use weak ferromagnets, so that ξ_F becomes larger. For instance, in a strong magnet like Co, ξ_F is of the order of 1 nm, while in the weak ferromagnet $\text{Pd}_{0.9}\text{Ni}_{0.1}$, ξ_F is larger and of the order of 10 nm.

Measurements of the quasi-particle DOS of FS bilayers have been conducted with both planar junctions and STS. Kontos *et al* measured tunneling spectroscopy with a series of planar junctions with F-layers both thinner and thicker than ξ_F .¹⁵³ This

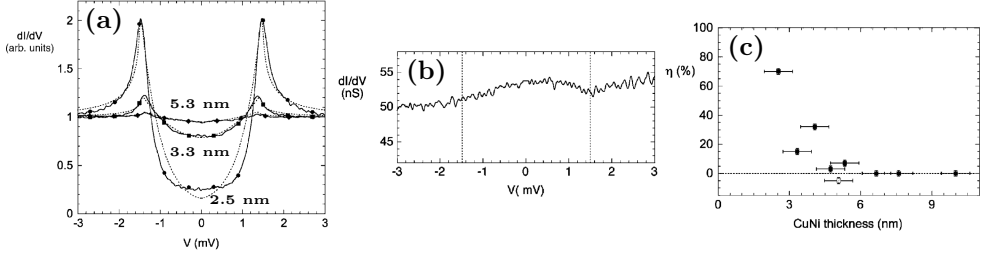


Figure 5.6: (a) Differential conductance measured with STM on three $\text{Cu}_{52}\text{Ni}_{48}/\text{Nb}$ bilayers with CuNi thicknesses as indicated. Broken line indicates calculated differential conductance. (b) Differential conductance measured on bilayer with 5.1 nm thick CuNi layer illustrating reversed DOS. (c) Plot of η (parameterized zero-bias (ZBC) conductance) versus CuNi film thickness. $\eta = 100\%$ corresponds to fully gapped or zero ZBC, while $\eta = 0\%$ corresponds to completely flat or normal metal ZBC. In this scheme, $\eta > 0\%$ corresponds to the 0-state and $\eta < 0\%$ corresponds to the π -state or inverted DOS. Taken from Ref. 154

allowed them to measure tunneling spectroscopy in both the 0 and π states. They used a weak ferromagnet, PdNi with 10% Ni, for the F-layer because at this composition PdNi has a relatively small exchange energy, $E_{ex} \sim 15$ meV, and thus a relatively large coherence length, $\xi_F \sim 45$ Å. This means that a bilayer with F-layer $d_F < 45$ Å should be in the 0-state while one thicker than ~ 45 Å should be in the π -state. Examples of their tunneling spectroscopy from bilayers with different d_F are shown in Fig. 5.5. It is clear from this data that the $d_F = 50$ Å junction spectroscopy is gapped, with a ZBC < 0 , while the $d_F = 75$ Å junction spectroscopy is inverted or gapless, with a ZBC > 0 . They found that the ZBC from their series of planar junctions followed this trend; $d_F < \xi_F$ implies gapped spectroscopy with ZBC < 0 , while $d_F > \xi_F$ implies inverted spectroscopy with ZBC > 0 . A plot of their ZBC versus d_F is shown in Fig. 5.5(b). Also apparent in this plot is the overall exponential decay of the pairing potential. In the 0-state ZBC and hence the gap extends as deep as ~ 0.978 , while in the π -state the ZBC never exceeds ~ 1.0025 .

Following this, STS studies were performed by Cretinón *et al* on a dilute ferromagnetic alloy, this time CuNi.^{154,155} Again a weak ferromagnet was used to maximize ξ_F and permit the use of a technologically convenient film thickness. As before with planar tunnel junctions, the strategy was to fabricate a series of films with a range of d_F both thicker and thinner than ξ_F so as to observe the shift from 0 to π state via the corresponding change in tunneling spectroscopy from gapped to inverted. They were very successful in observing the decay of the ZBC and gap in the 0 state, but were only marginally successful at measuring inverted tunneling spectrum in the π state. Tunneling spectra measured on some of their films are shown in Figs. 5.6(a) and (b), and a plot of parameterized ZBC (η) versus d_F is shown in Fig. 5.6(c). In Fig. 5.6(c) the ZBC is parameterized such that a gap corresponds to $0\% < \eta \leq 100\%$,

a flat spectrum corresponds to $\eta = 0\%$, and an inverted spectrum corresponds to $\eta < 0\%$. With the exception of the tunneling spectrum shown in Fig. 5.6(b), all of the spectra are either gapped or flat. This data shows that bilayers with d_F thinner than about ξ_F (5 nm in this case) were gapped, while those thicker than ξ_F were flat.[†] With one exception, they found the spectra to be spatially homogeneous at each d_F , a feature they attributed to the flatness of their films. That exception was a bilayer with $d_F = 5.1$ nm [Fig. 5.6(b)]. On that film they measured mostly flat tunneling spectra except in one area of the film where they measured π -state inverted spectra but only fleetingly. They note that, although the spectra were not reproducible, the presence of kinks in the spectra at close to the Nb superconducting gap (± 1.5 meV, indicated by broken vertical lines) led them to believe these inverted spectra were indeed proximity-related, and not a fortuitous artifact of unrelated cause.

The next challenge was to measure the π -state in FS bilayers with a strong ferromagnet ($E_{ex} \gg \Delta$). Several attempts have been made with planar tunnel junctions.^{156,157} Given the larger exchange energy, these measurements must be made with very thin F-layers in order to observe the π -state at $d_F \sim \xi_F$. In one of these measurements, Raymond *et al* used $\text{Co}_{0.6}\text{Fe}_{0.4}$, a strong ferromagnet with $E_{ex} \sim 100$ meV, in a FS planar tunnel junction. Spectra measured on these junctions were gapped for $d_F < 1$ nm (where $\xi_F \sim 1$ nm), becoming only weakly gapped for bilayers with $1 \leq d_F \leq 2.5$ nm. For films thicker than this, the spectra were essentially flat, and they found no evidence of the π -state. Following this, the same group measured another FS bilayer with a planar tunnel junction, this time with Ni as the strong ferromagnet.¹⁵⁷ With these measurements they observed evidence of the π -state in the form of an inverted DOS at zero bias. Unlike the earlier report on weak-ferromagnet FS junctions from Kontos *et al*,¹⁵³ the inverted zero-bias DOS has an additional mini sub-gap feature. They were unable to explain the sub-gap and suggested it represented new physics.

5.2 Materials and methods

For this research, CuNi was chosen as the weak ferromagnet. Samples grown with the same target and under nominally identical process conditions were measured with Rutherford backscattering spectrometry and determined to have an actual composition of $\text{Cu}_{43}\text{Ni}_{57}$ and a T_{Curie} of 150 K.¹⁵⁸ At this composition, the crossover to the π state can be estimated from the T_c versus F-layer thickness measurements [$T_c(d_F)$], where the minimum $T_c(d_F)$ signals the on-set of the π state. For $\text{Cu}_{43}\text{Ni}_{57}$ this cross-over should occur at about 3.5-4.0 nm.¹⁵⁹

The Nb/CuNi bilayer was grown by dc-magnetron sputtering in an ultra high vacuum system with base pressure of 10^{-9} mBar. The Nb and CuNi layers were sputtered from pure Nb and $\text{Cu}_{50}\text{Ni}_{50}$ (atomic %) targets at room temperature in 4 μ bar of pure Ar gas. The bilayer was grown with the Nb layer adjacent to the Si(100)

[†]Although the 5.3 nm d_F film [shown in Fig. 5.6(a)] is gapped yet is slightly thicker than ξ_F , the size of the error bars on its thickness [see Fig. 5.6(c)] suggests that this observation is still correct.

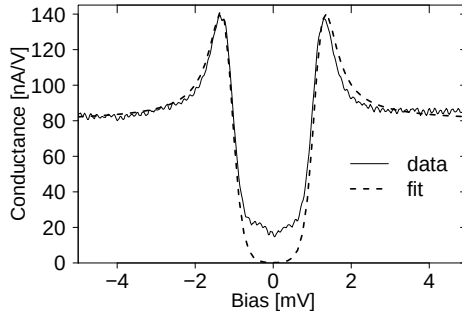


Figure 5.7: STS measured on Nb film in UHV STM at $T = 1.2$ K, with set point 1.5 mV, 100 pA. Fit parameters $\Delta = 1.12$ mV and $T_{eff} = 1.65$ K.

substrate and capped with the CuNi layer. All STM measurements were, therefore, made on the upper surface of the CuNi layer. The layer thicknesses were measured with low-angle X-ray reflection and found to be 27.9 nm and 3.5 nm for the Nb and CuNi layers, respectively, where the CuNi layer thickness was chosen to coincide with where the π state should set in.

All STM measurements were performed in a UHV STM with base pressure of 4×10^{-10} mbar. Point spectroscopy was measured by disengaging the STM feedback and then sweeping the bias voltage while measuring the tunneling current. Differential conductance (dI/dV) was determined by numerically differentiating the measured current versus voltage (IV) curve. Up to 50 IV 's were measured at each location and averaged before the dI/dV was calculated. See Section 2.7 for further details concerning STS measurements. The film was measured without post-growth etching or annealing.

The measurements in this Chapter were all made at a nominal temperature of around 0.75 K. This finite temperature along with any nonthermal noise will produce thermally smeared spectra, and this must be incorporated into the theoretical model fits that will be made in Sec. 5.4. How this is accomplished is best explained with the example of a Nb superconducting gap measured in the same UHV STM used for the measurements in this Chapter. In this example, a BCS quasiparticle density of states—appropriate for Nb—is used. The appropriate DOS for CuNi will be discussed in Sec. 5.4.

The BCS superconducting DOS (ρ_{BCS}) normalized to the DOS in the normal state (ρ_0) is given by,^{7,160}

$$\frac{\rho_{BCS}(E)}{\rho_0} = \begin{cases} \frac{E}{\sqrt{E^2 - \Delta^2}} & \text{if } E > \Delta, \text{ and} \\ 0 & \text{if } E < \Delta, \end{cases} \quad (5.1)$$

where E is energy and Δ is half the superconducting gap width. The differential conductance is then calculated using this DOS and a finite-temperature Fermi-Dirac

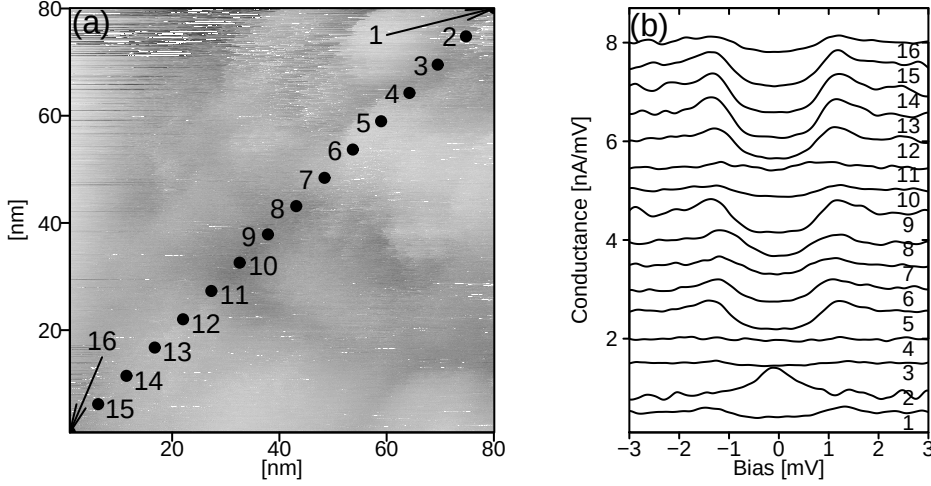


Figure 5.8: (a) Topography and (b) differential conductance measured simultaneously on Nb/CuNi bilayer with STM (measured at ~ 0.75 K, set point -2 mV and 1 nA). Numerical labels on differential conductance correspond to locations indicated in (a). Vertical scale of (a) is illustrated by a section shown in top of Fig. 5.9.

distribution function $[f(E - eV, T)]$,^{7,161}

$$\frac{d}{dV}I(V, T) = \int_{-\infty}^{\infty} \rho_t \rho_s(E, T) \frac{d}{dV} f(E - eV, T) dE, \quad (5.2)$$

where ρ_t is the tip DOS (presumed to be flat),[†] ρ_s is the DOS from Eq. 5.1, and V is the bias voltage. The fit is made iteratively, with Δ and T chosen to best fit of the measured dI/dV . An example fit along with measured spectrum is shown in Fig. 5.7. The measured dI/dV comes from a Nb sample taken with the UHV STM at a measured $T = 1.2$ K, while the parameters for the fitted curve are $\Delta = 1.12$ mV and $T_{eff} = 1.65$ K. This difference between the temperatures likely comes from a combination of inadequate thermal anchoring of wiring and insufficient RF-noise filtering.⁷

5.3 Results

Both topographic and spectroscopic measurements were made on the Nb/CuNi bilayer. An example of topography and simultaneously measured spectroscopy is shown in Figs. 5.8(a) and (b), respectively. This measurement was made at ~ 0.75 K with

[†]In this case the sample is superconducting while the tip is a normal metal. This calculation works equally well if the tip is superconducting and the sample not.

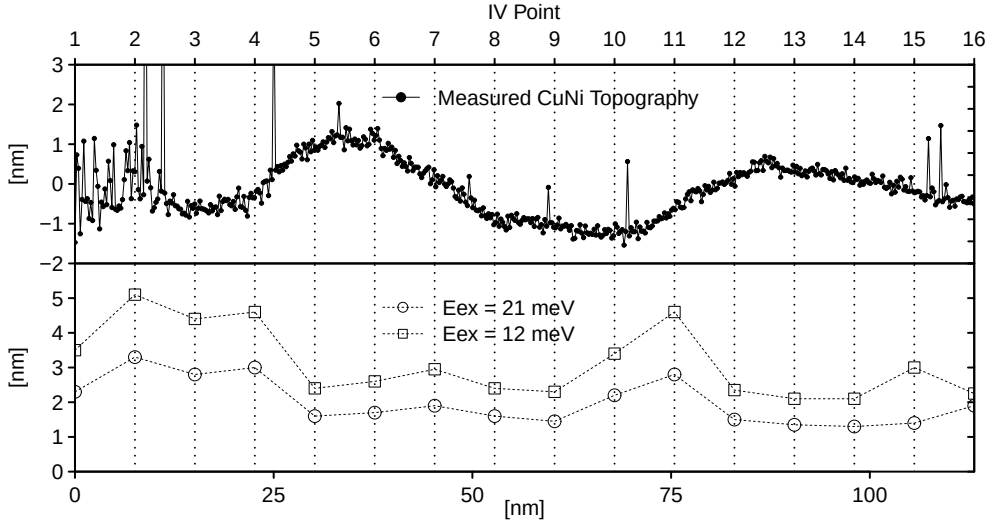


Figure 5.9: (●) Section through topography shown in Fig. 5.8(a) along the same diagonal as the indicated tunneling spectra. Numerical labels along the top axis indicate the position of each tunneling spectrum and correspond to the tunneling spectra shown in Fig. 5.8(b). d_F value used in model fit to Fig 5.8(b) data with $E_{ex} = 12$ meV ($\square$) and $E_{ex} = 21$ meV ($\circ$).

the same set-point (-2 mV and 1 nA) used for both topography and spectroscopy. During the topographic measurement, the scan was paused at set locations and IV 's were measured. In this example, 16 IV 's were measured along a diagonal at the locations indicated. The numerical labels in Fig. 5.8(b) indicate the position in Fig. 5.8(a) where each tunneling spectrum was measured. There appear to be a range of spectra from gapped (Nos. 1, 3-10, 12-16), to approximately flat (No. 11), and inverted (No. 2).

A section through the topography of Fig. 5.8(a) is shown in Fig. 5.9 (●). It was taken along the diagonal where the tunneling spectroscopy was measured, and the position where each was measured is indicated along the top axis. The film appears to be quite rough, with peak-to-peak (p-p) variations of up to ~ 2.5 nm. This is substantial for a 3.5 nm thick CuNi layer, but of course this roughness stems from both the Nb and CuNi layers. Fig. 5.9 will be discussed in more detail in Sec. 4.5.

Since the gap depth should decrease with F-layer thickness, if the surface topography was representative of d_F , then the gap should be shallower on higher parts of the film. In fact the gap depth is almost anti-correlated with what would be expected were this true. Specifically, spectra Nos. 5 and 6 have deeper gaps, yet were measured on the highest point of the topography. The deepest gaps should be measured in the zero-phase where the F-layer is thinnest. Spectra Nos. 3 and 4 have very

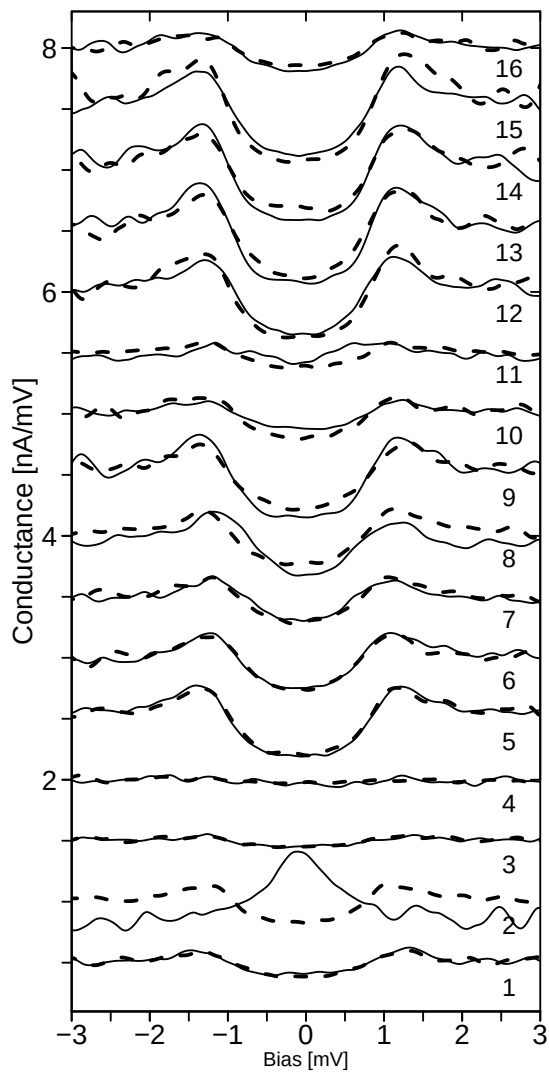


Figure 5.10: Tunneling spectroscopy from Fig. 5.8(b) (solid line) plus spectroscopy measured immediately afterwards in the same location and with same tunneling set point as used in Fig. 5.8 (broken line).

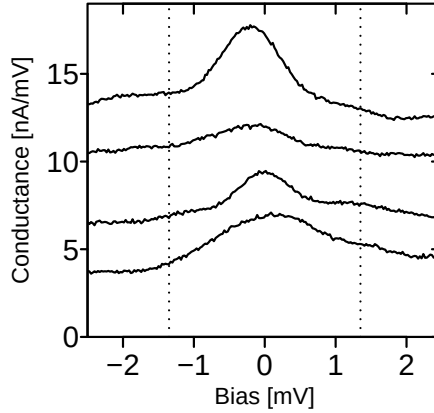


Figure 5.11: Examples of inverted tunneling spectroscopy. Measured at ~ 0.75 K, set point 2 mV and 1 nA.

weak gaps—are almost flat—yet correspond to a dip in the CuNi topography. Flat spectra would be expected at either the cross-over thickness between the zero and π phase or on a very thick F-layer where the OP has substantially decayed. Finally, inverted spectra should be measured on a thicker part of F-layer in the π phase, yet an inverted spectrum, spectrum No. 2, was measured at an intermediate height of the topography.

Immediately following the measurement displayed in Fig. 5.8, another measurement was made under the same tunneling conditions. The tunneling spectra from this second measurement (broken line) are shown in Fig. 5.10 along with the tunneling spectra from the first measurement (solid line). While most of the spectra are very similar, the inverted DOS seen in the first scan is gone and replaced by a gapped DOS. The topography measured during the first and second scans is very similar (topography from second scan is not shown), suggesting that there was very little drift between measurements. This plus the similarity of most of the spectra also suggests that the spectra in the two measurement were made at close to the same locations. No other inverted DOS spectra appear during subsequent measurement in the same area. Much like Cretinón *et al*, the inverted DOS spectrum was fleeting.^{154,155}

Measurements at other locations also revealed occasional inverted-DOS spectra. Examples of these are shown in Fig. 5.11. These inverted-DOS spectra were also not reproducible. Subsequent measurements at the same location produced only flat or gapped spectra. The broken vertical lines indicate ± 1.35 meV, the gap width, Δ , used in the theoretical model fit shown in Fig. 5.12 and discussed below. In all four of these inverted spectra there is no noticeable feature at $\pm \Delta$. This is unlike the inverted DOS measured by Kontos *et al* shown in Fig. 5.5(a), where there is a distinct notch or gap at $\pm \Delta$. A similar, though not as sharp, notch is apparent in the example inverted DOS measurement by Crétinon *et al* shown in Fig. 5.6(b). Lacking this characteristic

notch on either side of the inverted DOS brings into question whether the inverted DOS measured here are related to the π phase. It should be said, though, that the upturn does begin at $\pm\Delta$. Further, the height of a π -state inverted DOS should also be greatly diminished because of the overall decay of the OP. Compare the height of the inverted DOS to the plot of ZBC from Kontos *et al* shown in Fig. 5.5(b). In these measurements the magnitude of the ZBC in the π phase (where $N(0) > 1$) is significantly smaller than the magnitude of the ZBC in the zero phase (where $N(0) < 1$). The four inverted-DOS spectra shown in Fig. 5.11 are too tall to be consistent with an exponential decay of the OP.

5.4 Discussion

To try and understand the measured DOS versus the CuNi topography profile, a theoretical model was fitted to the data. The model used here is the same as the one described by Cr  tinon *et al.*¹⁵⁴ and used to analysis gap variations in Nb/CuNi bilayers, and subsequently used by Raymond *et al.*¹⁵⁶ to analyze tunnel junctions based on Nb/CoFe. It starts with the Usadel equation in the F layer which describes the Green function Θ for the pair correlations and is given by,

$$-\frac{\hbar D_F}{2} \frac{\partial^2 \Theta}{\partial x^2} + (\omega + iE_{ex}) \sin \Theta + \frac{1}{\tau_s} \sin \Theta \cos \Theta = 0, \quad (5.3)$$

with D_F the electronic diffusion constant in the F-layer, ω the Matsubara frequency, and τ_s the magnetic scattering time, which can be related to a magnetic scattering length by $L_s = \sqrt{\hbar D_F \tau_s}$. In this formalism, the DOS is given by $\text{Re}[\cos \Theta(\epsilon)]$. The Usadel equation is solved for the case of F-layer of thickness $x = d_F$ (where the pair correlation function goes to zero) under the assumption of full interface transparency. According to Ref. 156, the Usadel equation then yields,

$$\Theta_{d_F} = \frac{8}{\sqrt{1-p^2}} \exp \left(-\sqrt{i + \tilde{\gamma} + i\tilde{\omega}(x/\xi_F)} \right) \sqrt{\frac{\sqrt{1-p^2 \sin^2 \frac{\Theta_0}{2}} - \cos \frac{\Theta_0}{2}}{\sqrt{1-p^2 \sin^2 \frac{\Theta_0}{2}} + \cos \frac{\Theta_0}{2}}}, \quad (5.4)$$

where $p^2 = 1/(1 + i/\tilde{\gamma})$, $\tilde{\omega} = E/E_{ex}$, $\tilde{\gamma} = 1/(\tau_s E_{ex})$, and $\cos \Theta_0 = |E|/\sqrt{E^2 - \Delta^2}$. The resulting calculated spectrum was then thermally broadened using Eq. 5.2 at an effective temperature (T_{eff}) in the same manner as described in above in Sec. 5.2.

Fits to all of the spectra shown in Fig. 5.8(b) were made with Eq. 5.4. One of these spectra, No. 5, is shown Fig. 5.12(a) (solid line) along with a theoretical fit (broken line). This theoretical fit was made using fitting parameters $\Delta = 1.35$ mV, $D_F = 5 \times 10^{-4}$ m²/s, $T_{eff} = 1.2$ K, $L_s = 1.3$ nm, $d_F = 1.6$ nm, and $E_{ex} = 21$ meV. Of these parameters D_F was taken from the literature,¹⁶² while Δ and T_{eff} were adjusted to provide the best overall fit of the spectra and then fixed at those values. $\Delta = 1.35$ meV produced the best fit to the coherence peaks for all fitted spectra. The same value was used by Ref. 156 while a larger value, $\Delta = 1.5$ meV, was used by

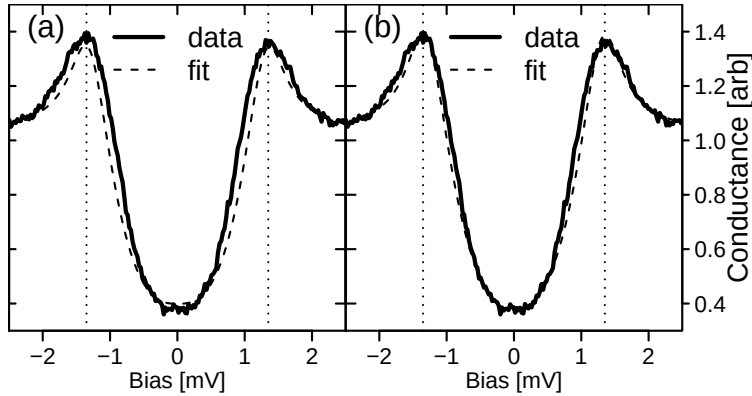


Figure 5.12: (solid line) Spectrum No. 5 from Fig. 5.9. (broken line) Fits to theoretical model Eq. 5.4 with (a) $E_{ex} = 21$ meV ($L_s = 1.3$ nm, $d_F = 1.6$ nm, $T_{eff} = 1.2$ K) and (b) $E_{ex} = 2$ meV ($L_s = 2.0$ nm, $d_F = 2.4$ nm, $T_{eff} = 1.2$ K).

Ref. 154. The E_{ex} value for the fit in Fig. 5.12(a) was estimated from the π -state cross-over thickness of 4 nm (discussed above) using $d_F \sim \xi_F$, while L_s and d_F were freely adjusted to best fit the measured spectra.

Similar fits were made to spectra Nos. 1, 3–4, 6–10, 12–16, but with all parameters fixed at the values used in Fig. 5.12(a) except for d_F . For each spectrum, d_F was adjusted to find the best fit. Spectrum No. 2 was excluded because it was inverted and could not be fitted with any physically reasonable parameters (see discussion below). This difficulty was also noted in Ref. 154. Another spectrum, No. 11, was also excluded because it was essentially flat and a fit was not possible. While what is a good fit is quite subjective, the criteria used here was a good match to both the gap width and depth. Most fits could be improved by small changes to T_{eff} , E_{ex} , or L_s , but not in a way consistent across all fitted spectra.

These d_F values were then taken as the local F-layer thickness, and are plotted in Fig. 5.9 (o). These values range from 1.3 to 3.3 nm, with a mean value of 2 nm, significantly less than the measured thickness of the CuNi layer, 3.5 nm, suggesting that this calculated thickness is not a good fit to the data.

Although $E_{ex} = 21$ meV is a reasonable value based upon the estimated value from CuNi properties, all of the fits are improved by fitting profiles with a smaller E_{ex} . This can be seen in Fig. 5.12(b) which was fitted with $E_{ex} = 2$ meV. This value, though, is smaller than is physically reasonable. Other researchers also noted that best-fit E_{ex} values were typically less than those taken from other independent estimates.¹⁵⁶ An important point about comparing the fits in Figs. 5.12(a) and (b) is that the L_s values in these two fits are different. This was necessary to produce reasonable fits. More will be said about this below.

A second estimate of local d_F 's was made using $E_{ex} = 12$ meV ($L_s = 2.0$ nm),

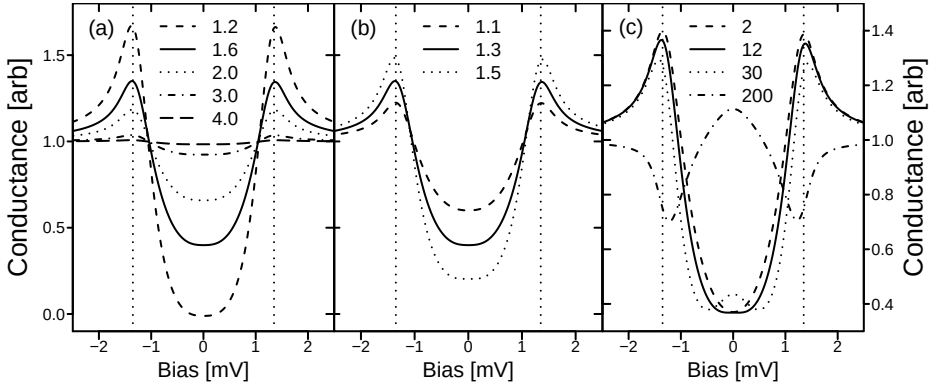


Figure 5.13: Fits to theoretical model Eq. 5.4. (a) Varying d_F [nm] as indicated ($E_{ex} = 21$ meV, $L_s = 1.3$ nm, $T_{eff} = 1.2$ K) (b) Varying L_s [nm] as indicated ($E_{ex} = 21$ meV, $d_F = 1.6$ nm, $T_{eff} = 1.2$ K). (c) Varying E_{ex} [meV] as indicated ($L_s = 2.0$ nm, $d_F = 2.4$ nm, $T_{eff} = 1.2$ K).

where E_{ex} is the same as used by Cr  tinon *et al.*¹⁵⁴ for a similar CuNi alloy. The resulting F-layer thickness profile is shown of Fig. 5.9 ($\square$). This profile produces a thicker F-layer that is closer to the measured 3.5 nm thickness, with values ranging from 2.1 to 5.1 nm, and a mean of 3.1 nm. If these d_F data are combined with the measured topography shown in Fig. 5.9 (top) to estimate the FS-interface profile, the result is an Nb layer with variations of ~ 4.3 nm p-p. This is rougher than the 2 nm p-p topography variations measured by AFM on a Nb film grown immediately following the CuNi/Nb bilayer growth and rougher than Nb films typically grown under the same process conditions. From this it seems like a reasonable model of F-layer thickness and FS-interface smoothness cannot be accomplished by only varying d_F with fixed E_{ex} and L_s .

To better understand the effect of varying parameters d_F , L_s , and E_{ex} , calculations were made for each of these parameters with all other parameters fixed. The resulting spectra are shown in Figs. 5.13(a), (b), and (c) for parameters d_F , L_s , and E_{ex} , respectively. As has already been demonstrated in the FS-interface calculations shown above, varying d_F produces large variations in gap depth, ranging from a true gap for $d_F = 1.2$ nm to an almost flat DOS at $d_F = 4.0$ nm. Increasing d_F beyond this does not produce an inverted DOS as was noted above. Varying L_s also produced variations in the gap depth, with smaller values—equivalent to increased spin scattering—producing shallower gaps as more pairs are broken over a given F-layer thickness. If L_s is small enough it should dominate other pair-breaking mechanisms and should cause both the OP to decay faster and the oscillation period to increase.^{163,164} While the increased OP decay was observed with increased L_s , no evidence was seen that increasing or decreasing L_s produced any evidence of inverted DOS, the signature of the π state.

Unlike the case of d_F and L_s , varying E_{ex} did produce an inverted DOS. For small values, increasing E_{ex} from 2 meV initially increased the gap width (compare 2 meV curve to 12 meV curve), while at larger E_{ex} , a small in-gap peak appeared (just visible even at $E_{ex} = 12$ meV).[†] This peak continued to grow as E_{ex} was increased, resulting in a ZBC ~ 1 at $E_{ex} \sim 140$ meV, and a well developed inverted DOS—with ZBCP and inverted coherence peaks—at higher values still (see $E_{ex} = 200$ curve). Unfortunately this inverted DOS could not be combined with variations in d_F or L_s to produce a transition from deeply gapped, to flat, to inverted DOS. Starting with an inverted DOS, decreasing d_F (increasing L_s) did not produce a gapped spectrum, while increasing d_F (decreasing L_s) served only to decrease the ZBCP height and inverted coherence peak depth. The evidence from these calculations is that the model is not suitable to capture in full the phenomena observed here and by other researchers (Ref. 153,154), and cannot be used to explain the seemingly counterintuitive measurements observed here.

But what is the cause of variations in the measured spectra? One possibility is that the CuNi alloy is not homogeneous and that Ni-rich clusters have formed. In locally Ni-rich regions E_{ex} will be larger while in Ni-poor regions it will be smaller. Variations in E_{ex} will be reflected in variations in ξ_F which will change the local Andreev pair DOS at the F-layer surface. Thus, even for a flat CuNi film with constant thickness, variations in spectra would be observed. In terms of the bilayer measurements presented here, that would mean that the flat spectra (Nos. 3, 4, 10, 11, and 16) measured at low parts of the topography were measured over Ni-rich regions, while the gapped spectra (Nos. 5, 6, 12, 13, and 14) measured over high points in the topography were measured over locally Ni-poor regions. This would account for the apparently anti-correlation between the CuNi-layer surface profile and the character of the measured spectra.

CuNi films are known to be inhomogeneous. Measurements of S/F/S trilayers with $\text{Cu}_{1-x}\text{Ni}_x$ F-layers showed broader transition temperatures than similar trilayers with $\text{Pd}_{1-x}\text{Ni}_x$ F-layers.¹⁶⁵ This broadening of the transition temperature was attributed to the greater propensity of Ni-rich clusters to form in $\text{Cu}_{1-x}\text{Ni}_x$ than in $\text{Pd}_{1-x}\text{Ni}_x$.^{165,166} Other researchers have explained high-temperature magnetic susceptibility measurement of $\text{Cu}_{1-x}\text{Ni}_x$ thin films in terms of Ni-rich clusters.¹⁶⁷ These clusters, estimated to be on the order of 5-10 nm, would produce regions of the film with a larger E_{ex} values. Similar Ni-clusters have also been detected in bulk samples via neutron-scattering and high-temperature susceptibility measurements.¹⁶⁸ One way to investigate variations in E_{ex} would be to repeat the calculation of Nb film roughness but with E_{ex} as the free parameter rather than d_F . In principle, varying E_{ex} should produce variations in gap depth much as varying d_F did, in practice, as was discussed in reference to Fig. 5.13(c), the model used was not capable of producing these variations.

[†]This peak was seen by other researchers using this model (see Fig. 7 in Ref. 156)

5.5 Conclusion

STS on a weak ferromagnet/superconducting ($\text{Cu}_{43}\text{Ni}_{57}/\text{Nb}$) bilayer produced a range of tunneling spectra from gapped to flat. These spectra were consistent with spectra measured by other researchers. A theoretical model was fitted to the gapped data with d_F as free parameter. These estimates of d_F were used to estimate the CuNi-layer thickness and combined with the measured CuNi-layer topography were used to estimate the Nb/CuNi-interface profile. Using a larger E_{ex} value (21 meV), the estimate of the CuNi film thickness proved to be smaller than the thickness measured by X-ray. Fits to the model with a smaller E_{ex} value (12 meV) produced a CuNi-layer that was approximately equal to the measured CuNi thickness, but when combined with the measured CuNi topography, produced an FS-interface profile rougher than Nb films grown under nominally identical conditions. This suggests that both the CuNi-layer thickness and its material properties—both of which could produce the variation in spectra measured on this film—vary laterally across the film. Because there is much evidence of Ni-clusters forming in both bulk and thin-film CuNi, an inhomogeneous CuNi alloy with Ni-rich clusters could explain the variations in material properties. These variations in Ni-concentration could produce variations in E_{ex} that could easily explain variations in the spectra measured here.

Some inverted-DOS spectra were measured intermittently on the CuNi layer. The origin of the inverted DOS is unknown. Because of the extraordinary height of the ZBC of some of the inverted DOS and because of a lack of significant features at the gap-width, it is difficult to be confident that these inverted DOS spectra are conclusive evidence of the π state.

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Summary

This thesis presents scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements performed on the surface of thin-films of metallic manganites, cobaltite oxides, and on the ferromagnetic surface of ferromagnetic /superconducting (FS) bilayers. In all cases, the local electronic density of states (LDOS) of these samples is mapped from both numerically differentiated current-versus-voltage curves and from conductance maps made using a lock-in amplifier. This could be done at different temperatures between about 330 and 1 Kelvin, and in magnetic field up to a few Tesla. The aim is to connect salient features in the LDOS to the physics of the systems under consideration. With STM/S the sample surface's electronic properties can be mapped with nanometer or finer resolution, providing one of the advantages over other techniques such as planar-junction tunneling spectroscopy. Specifically, in the oxide systems there is the question whether electronic phase separation (a spatial separation of metallic and insulating areas in the sample) can be found and connected to the presence of the metal-insulator transition (in the manganites), or an intrinsically low-temperature inhomogeneous state (in the cobaltites). A related question is whether and how the local electronic properties change under influence of an applied magnetic field. In the case of the FS bilayers, the issue is whether the signature of an inhomogeneous superconducting order parameter, which is known to be induced in the ferromagnet by the proximity of the superconductor, can be found.

Chapter 1 provides a general introduction to the thesis

Chapter 2 provides a brief description of the experimental equipment, and an introduction to STM and STS along with details of some salient features of the underlying technology. This includes a discussion of the issues of the coarse approach of tunneling tip to sample surface, and the amplification of the weak tunneling currents.

Chapter 3 presents STM/S measurements of thin-films of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ with the goal of exploring how film morphology and substrate-induced strain relate to electronic homogeneity. The results of these measurements can be divided into two groups based upon the film surface morphology alone: flat and rough surfaces. Flat films are characterized by atomically smooth terraces, with unit-cell step heights between terraces. Rough films are characterized as having no apparent terraces and no apparent unit-cell step heights. STS measurements indicate that flat films are electronically homogeneous while rough films are electronically inhomogeneous. Flat films were also electronically inactive, with tunneling spectra unaffected by changes in temperature or applied magnetic field. Rough films, on the other hand, responded to an applied magnetic field, displaying an overall increase in metallic areas with

increasing field, consistent with the percolation model of colossal magnetoresistance. Substrate-induced strain was shown to play no role in electronic homogeneity. It seems likely that films of this material with flat surfaces have undergone a change in electronic structure as compared to the bulk, driven by the change in symmetry.

Chapter 4 presents STM/S measurements on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSCO) films with $x = 0.5$, for the purpose of exploring the relationship between film thickness and electronic homogeneity. These results show that film thickness drives the electronic homogeneity of cobaltite films. Evidence from the literature indicates that bulk LSCO with $x \leq 0.18$ is electronically inhomogeneous, while bulk LSCO with $x > 0.18$ is not. Published magnetoresistance and small angle neutron scattering measurements have demonstrated that thin film LSCO, even for $x = 0.5$, is inhomogeneous if thinner than a critical thickness (t^*) of about 8 nm. In this chapter STS measurements show that the film that we studied which was thinner than t^* was electronically inhomogeneous, with metallic grains ranging from 5 to 30 nm that form clusters of up to 100 nm in size; while the film that was thicker than t^* was homogeneous, with uniform electronic properties. As both films were rough, with no apparent atomically smooth terraces, this indicated that the surface morphology plays no role in the inhomogeneity. The STM data indicate that the metallic clusters detected on the electronically inhomogeneous film are magnetic since they are sensitive to an applied magnetic field. Overall, the data are consistent with a picture of the inhomogeneous film being composed of ferromagnetic clusters embedded in an insulating matrix, with some of those clusters being pinned and unresponsive to an applied field.

Chapter 5 presents STM/S measurements on a ferromagnetic/superconducting bilayer composed of a Nb film capped by a thin film of CuNi, a weak ferromagnetic alloy. These measurements were intended to probe the order parameter induced by the superconductor into the ferromagnet. This order parameter is expected to not only decay as a function of the distance from the FS interface (which is caused by the exchange energy of the ferromagnet) but also to oscillate; meaning that the quantum mechanical phase of the order parameter can switch from zero to π . The signature of this phase change is a change from a gapped quasiparticle DOS when the order parameter is positive (zero state) to an inverted DOS where the order parameter is negative (π state). Measurements of a rough FS bilayer display a variety of tunneling spectra from deeply gapped to flat. Inverted spectra were occasionally measured but were not reproducible. The zero-bias maximum of these inverted spectra were too large and did not have a characteristic dip or kink at the gap energy as seen in planar junctions, making it questionable whether these inverted spectra were evidence of the π -phase. Model fits to gapped spectra are used to estimate the local F-layer thickness. Combined with the measured F-layer topography, the local F-layer thickness can be used to estimate the morphology of the underlying Nb layer. This calculated morphology was significantly rougher than typical Nb films grown under identical conditions. This suggests that other factors contribute to the measured variation in the spectra. A likely candidate is Ni-clustering. Such Ni-clusters would lead to variations in the exchange energy that could in turn produce the spectra variations seen in these measurements.

Samenvatting

Dit proefschrift beschrijft rastertunnelmicroscopie (STM) en rastertunnelspectroscopie (STS) experimenten aan de oppervlakken van dunne films van metallische manganaten, cobaltiet oxides en op het ferromagnetische oppervlak van ferromagnetische/supergeleidende (FS) dubbellagen. Voor deze materiaalsystemen is de lokale elektronische toestandsdichtheid (LDOS) ruimtelijk in kaart gebracht, zowel door het numeriek differentiëren van de stroom-spannings curve als door het maken van geleidingsafbeeldingen met een *lock-in versterker*. Het was mogelijk dit te doen bij temperaturen tussen circa 330 en 1 Kelvin en in magneetvelden tot enkele Tesla's. Het doel is steeds om de kenmerkende eigenschappen van de LDOS in verband te brengen met de fysica van het te bestuderen materiaalstelsel. Met STM/S is het mogelijk het preparaatoppervlak af te beelden met een resolutie kleiner dan één nanometer; dit is een van de voordelen van deze techniek boven andere technieken zoals tunnelspectroscopie aan planaire juncties. In het geval van de oxidische materiaalsystemen gaat het hierbij om de vraag of elektronische fasescheiding (het bestaan van ruimtelijk gescheiden metallische en isolerende gebieden in het preparaat) waargenomen kan worden en gekoppeld kan worden aan de aanwezigheid van de metaal-isolator overgang (in de manganaten) of aan een intrinsiek inhomogene toestand bij lage temperatuur (in de cobaltiet oxides). Een gerelateerde vraag is of en hoe de lokale elektronische eigenschappen veranderen onder de invloed van een aangelegd magneetveld. Voor de FS-dubbellagen is er de onderzoeksvraag of de signatuur van een inhomogene supergeleidende ordeparameter, waarvan bekend is dat deze in de ferromagneet geïnduceerd wordt door de nabijheid van de supergeleider, gevonden kan worden.

Hoofdstuk 1 bevat een algemene inleiding tot dit proefschrift.

Hoofdstuk 2 geeft een korte beschrijving van de experimentele apparatuur waarna een inleiding volgt tot de technieken STM en STS alsmede tot enkele belangrijke aspecten van de onderliggende technologie. Daarbij gaat het onder andere om de details van het grofnaderingssysteem waarmee de tunneltip en het preparaatoppervlak in elkaars nabijheid worden gebracht en om de versterking van de (zeer zwakke) tunnelstroom.

In **Hoofdstuk 3** worden STM/S-metingen aan dunne films van $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ gepresenteerd met het doel te onderzoeken hoe film morfologie en substraat geïnduceerde vervorming gerelateerd zijn aan elektronische homogeniteit. De resultaten van deze metingen kunnen op basis van de morfologie van het filmoppervlak worden onderverdeeld in twee groepen: vlakke en ruwe oppervlakken. Vlakke films worden gekarakteriseerd door atomair vlakke terrassen, met eenheidscel-hoge stappen tussen de terrassen. Ruwe films worden gekenmerkt door de kennelijke afwezigheid van gedefiniëerde atom-

air vlakke terrassen en eenheidscel-hoge stappen. STS-metingen geven aan dat vlakke films elektronisch homogeen zijn terwijl ruwe films elektronisch inhomogeen zijn. Vlakke films bleken ook elektronisch inactief te zijn, waarbij de tunnelspectra niet beïnvloed werden door verandering van de temperatuur of het aangelegde magnetveld. Ruwe films integendeel reageren op een aangelegd magnetveld met een toename van de metallische gebieden bij toenemend veld, hetgeen consistent is met het percolatiemodel van kolossale magnetoweerstand. Substraat-geïnduceerde deformatie bleek geen invloed te hebben op de elektronische homogeniteit. Het lijkt waarschijnlijk dat vlakke oppervlakken een verandering in de elektronische structuur hebben ondergaan ten opzichte van de bulk, gedreven door een verandering in symmetrie.

In **Hoofdstuk 4** worden STM/S-metingen aan $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSCO) films met $x = 0.5$ gepresenteerd met het doel de relatie tussen filmdikte en elektronische homogeniteit te onderzoeken. De resultaten laten zien dat de filmdikte bepalend is voor de elektronische homogeniteit van cobaltiet films. Uit de literatuur kan worden opgemaakt dat bulk LSCO met $x \leq 0.18$ elektronisch inhomogeen is en bulk LSCO met $x > 0.18$ homogeen. Gepubliceerde magnetoweerstands- en lage-hoek neutronenverstrooiingsmetingen laten zien dat dunne LSCO films, zelfs voor $x = 0.5$, inhomogeen zijn wanneer ze dunner zijn dan een kritische dikte (t^*) van ongeveer 8 nm. In dit hoofdstuk laten STS-metingen zien dat een film dunner dan t^* elektronisch inhomogeen is met daarin metallische korrels die in grootte variëren van 5 tot 30 nm en die clusters vormen tot 100 nm grootte, terwijl een preparaat dikker dan t^* homogeen is met uniforme elektronische eigenschappen. Het feit dat beide films ruw waren, zonder gedefiniëerde atomair vlakke terrassen, geeft aan dat oppervlaktemorfologie geen rol speelt voor de elektronische inhomogeniteit. De STM-metingen geven aan dat de in de elektronisch inhomogene film waargenomen metallische clusters magnetisch zijn omdat ze gevoelig zijn voor een aangelegd magnetveld. De verzameling meetgegevens past bij het beeld van een inhomogene film die is samengesteld uit ferromagnetische clusters ingebed in een isolerende matrix maar waarbij sommige van deze clusters gepind zijn en niet reageren op een aangelegd veld.

In **Hoofdstuk 5** worden STM/S-metingen aan een FS-dubbellaag gepresenteerd. Deze dubbellaag is opgebouwd uit een laag Nb afgedekt met een dunne laag CuNi – een zwak ferromagnetische legering. Deze metingen hadden als doel de door de supergeleider in de ferromagneet geïnduceerde ordeparameter te onderzoeken. De verwachting is dat deze ordeparameter niet alleen afvalt als functie van de afstand tot het FS-grensvlak (hetgeen veroorzaakt wordt door de *exchange energie* van de ferromagneet) maar ook dat deze ordeparameter oscilleert; dit betekent dat de quantummechanische fase van de ordeparameter kan omschakelen van 0 naar π . Kenmerkend voor deze faseverandering is een verandering van een quasideeltjes toestandsdichtheid met een uitgesproken minimum (de supegeleidende 'gap' of kloof) zolang de fase nul is, naar een geïnverteerde toestandsdichtheid, met een maximum, als de fase π is. Metingen aan een ruwe FS-dubbellaag laten een variëteit aan tunnelspectra zien, van spectra met een diepe kloof tot vlakke spectra. Geïnverteerde spectra werden af en toe waargenomen maar waren niet reproduceerbaar. Het *nul bias maximum* van deze spectra was te hoog en had niet de karakteristieke dip of buiging bij de kloof-energie

zoals waargenomen in planaire tunneljuncties hetgeen het betwistbaar maakt of deze geïnverteerde spectra bewijs zijn voor de π fase. Uitgaand van de gemeten spectra die een kloof vertonen is middels extractie van modelparameters een schatting gemaakt van de lokale F-laagdikte. In combinatie met de gemeten F-laag topografie kan de lokale F-laagdikte gebruikt worden om een schatting te maken van de morfologie van de onderliggende Nb laag. Deze berekende morfologie was beduidend ruwer dan het oppervlak van typische Nb films die gegroeid worden onder gelijke condities. Dit suggereert dat er andere factoren zijn die bijdragen aan de gemeten variatie in de spectra. Een waarschijnlijke kandidaat-verklaring is de vorming van nikkel clusters. De aanwezigheid van zulke nikkel clusters zou namelijk resulteren in variaties in de exchange energie die op hun beurt de variaties in de spectra kunnen veroorzaken die in deze experimenten zijn waargenomen.

Curriculum vitae

- B.S. Mechanical Engineering, North Carolina State University, 1988.
- Master of Economics, North Carolina State University, 1990.
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