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**Magnetic Structure in Manganites as Probed by
Magnetic Force Microscopy**

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**Magnetic Structure in Manganites as Probed by
Magnetic Force Microscopy**

by

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Dissertation

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Dedicated to my family and friends in Austin.

Thanks for keeping me sane.

Acknowledgments

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Magnetic Structure in Manganites as Probed by Magnetic Force Microscopy

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Supervisor: Alex de Lozanne

This dissertation describes the use of magnetic force microscopy to directly measure the magnetic structure of a sample on a microscopic level. Our magnetic force microscope has been operated at temperatures ranging from 293 to 4.3 K and fields ranging from 0 to 3 T, providing a method for imaging temperature and field-dependent magnetic phase transitions and domain structures on a local scale. On the instrumentation side, I present details of the design, construction, and operation of a magnetic force microscope with coarse three dimensional tip/sample positioning. On the sample side, I focus primarily on the results of our studies concerning magnetic phase transitions in the manganite $\text{La}_{1-x-y}\text{Pr}_y\text{Ca}_x\text{MnO}_3$, which for some dopings is a colossal magnetoresistive material. I will briefly discuss two ongoing projects: the use of our magnetic force microscope to image field-dependent domain structure in patterned magnetic manganite films and its use as an electrostatic force microscope.

Table of Contents

Acknowledgments	v
Abstract	viii
List of Figures	xi
Chapter 1. Introduction	1
Chapter 2. Force Microscopy	3
2.1 Magnetic Force Microscopy	4
2.2 Magnetic Force (Gradient) Microscopy	6
Chapter 3. MFM Design and Operation Details	8
3.1 Cantilever	8
3.2 Scanner	11
3.3 Positioner	12
3.4 Support	14
3.5 Chamber	15
3.6 Electronics	17
3.7 Optical Alignment of Tip and Sample	19
3.8 Experimental Results	21
Chapter 4. Introduction to Manganite Physics	24
4.1 CMR effect	24
Chapter 5. An MFM Study of the Magnetic Structure in a CMR Film around the Insulator–Metal Transition	28
5.1 Experimental Setup	29
5.2 Temperature Dependent MFM data	32
5.3 Discussion	34

Chapter 6. An MFM Study of the Magnetic Structure in a CMR Single Crystal around a Glass-Like Transition	37
6.1 Chemical Pressure and Glassy Behavior	38
6.2 Experimental Setup	40
6.3 Temperature Dependent MFM data	43
6.4 Field Dependent MFM data	46
6.5 Discussion	47
Chapter 7. Thin-Film Manganite Devices	50
7.1 Magnetic Domain Walls in Manganites	50
7.2 MFM and Transport data	52
7.3 Questions	56
7.4 Micromagnetic Simulation	57
7.5 Future Direction	60
Chapter 8. Electrostatic Force Microscopy	62
8.1 Introduction to $\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3\text{:LuMnO}_3$	63
8.2 MFM/EFM Scans of $(\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3)_{0.2}(\text{LuMnO}_3)_{0.8}$	64
8.3 Future Direction	66
Bibliography	68
Vita	74

List of Figures

1.1	General SPM diagram	2
3.1	MFM diagram	9
3.2	Details of the MFM probe	10
3.3	“ x - y ” offset mechanism	13
3.4	Peg and slot rotational coupling from an x - y - z pipe to an x - y - z shaft	14
3.5	MFM pipe with integrated window	16
3.6	Lateral alignment of tip and patterned sample	19
3.7	Lateral alignment of tip and single crystal sample	20
3.8	MFM/AFM images of patterned permalloy element	21
3.9	MFM/AFM images of $\text{La}_{1/4}\text{Pr}_{3/8}\text{Ca}_{3/8}\text{MnO}_3$ single crystal	23
4.1	The perovskite structure	25
4.2	Crystal field splitting of Mn d -orbitals	26
4.3	Double exchange mechanism	26
5.1	The temperature-dependent resistivity of the LPCMO thin film	31
5.2	Topography and MFM at 120 K during warming	32
5.3	The temperature-dependent MFM image sequence for cooling, for warming, and the resistivity of the LPCMO thin film over a thermal cycle	33
6.1	Zero field topography and MFM images of the LPCMO single crystal at 6 K	41
6.2	MFM images of one area of the sample ($10 \times 10 \mu\text{m}^2$) and M vs. T during ZFC-FW	43
6.3	MFM images of one area of the sample ($10 \times 10 \mu\text{m}^2$) and M vs. H at various magnetic fields at 6.8 K after ZFC	45
6.4	Two-probe resistance of the sample taken in situ during MFM scans from Fig. 6.3	47

6.5	MFM image from Fig. 6.3(g) superimposed on a polarized optical microscope image	48
7.1	Order parameters across a magnetic domain wall	50
7.2	Optical image of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ domain wall device mounted inside the MFM	52
7.3	Optical image of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ domain wall device	53
7.4	Ex situ transport data of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ domain wall device at 77 K	54
7.5	MFM images and in situ transport data of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ domain wall device at 77 K	55
7.6	Micromagnetic simulation of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ device	58
7.7	Zoom-in of micromagnetic simulation result and MFM image showing vertical domain wall	59
7.8	Zoom-in of micromagnetic simulation result and MFM image showing diagonal domain wall	60
7.9	Vertical domain wall at a constriction with the inclusion of CO phase	61
8.1	Electrostatic Force Microscopy	62
8.2	Polarized optical microscope image of $(\text{LSMO})_{0.2}(\text{LMO})_{0.8}$ sample	64
8.3	Room temperature MFM/EFM scans of $(\text{LSMO})_{0.2}(\text{LMO})_{0.8}$ sample	65
8.4	EFM scan of $(\text{LSMO})_{0.2}(\text{LMO})_{0.8}$ sample at 77 K	66
8.5	Relative (to 4 K) dielectric loss tangent vs. temperature for HoMnO_3 and EFM contrast vs. temperature	67

Chapter 1

Introduction

The invention of the scanning tunneling microscope (STM) in 1982 [1] brought about a completely new way of thinking about how to answer questions in the field of surface science. In STM, a sharp metallic tip is scanned across a biased metallic sample and the tunneling current between the two serves as an extremely sensitive distance sensor. The direct, real-space visualization of atomic scale features and phenomena provided (and still provides today) the inspiration and approach for literally thousands of experiments. Soon after the introduction of the STM, people began to broaden the concept of a tunneling probe into a generic interaction probe (see Fig. 1.1). As long as the interaction volume can be miniaturized, any probe can be incorporated into a scanning probe microscope (SPM). The library of SPM interactions available today is truly immense, running the gamut from forces (electrostatic, magnetic, van der Waals, etc.) to optical spectroscopy to chemical interactions to thermal properties and beyond.

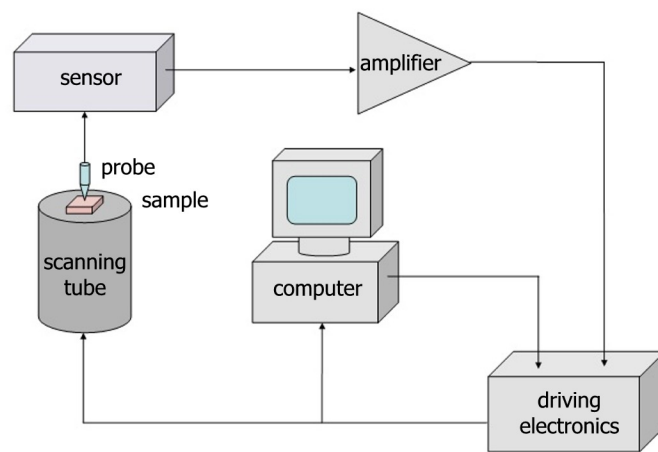


Figure 1.1: General SPM diagram. A scanner capable of three-dimensional motion scans a sample relative to a probe. The signal from the probe is amplified and sent to driving electronics that controls the scanner and sends image information to a computer. The user controls the driving electronics via the computer.

Chapter 2

Force Microscopy

The technique used in this dissertation, magnetic force microscopy (MFM)¹, is based on another SPM technique, atomic force microscopy (AFM). [2] In AFM, a tip serves as the probe for atomic-range forces in order to acquire the topography of a sample. The tip is attached to a cantilever with spring constant k which reacts to a deflection z with a force

$$F = -kz \tag{2.1}$$

in the direction perpendicular to the plane of the lever. All that is needed to sense the interaction of the tip and sample is a way to read out the deflection of the lever. A tunneling sensor fixed above the lever [2], a laser and split photodiode [3], a fiberoptic interferometer [4], and a piezoresistive [5] or piezoelectric [6] element embedded in the lever itself have all been used as deflection sensors.

Initially, two modes for acquiring topography naturally presented themselves. In the first mode, constant-plane scanning, the tip is brought into

¹For the sake of brevity, throughout this dissertation I will use the "M" at the end of any three letter acronym to refer to both the technique (microscopy) and the instrument itself (microscope).

contact and scanned in a plane roughly parallel to the sample surface. The cantilever deflects more over higher features on the sample and topography is identified with the cantilever deflection. One problem with this scanning mode is that the tip/sample force varies with topography changes. If the force is too high, the tip and/or sample may be damaged. In the second mode, these problems are somewhat mitigated by enabling a feedback loop during scanning that changes the overall tip/sample distance to keep the lever deflection constant. In this mode, since the deflection is constant, the force is constant, and the topography is identified with the overall tip/sample distance changes.

2.1 Magnetic Force Microscopy

MFM can be performed in a mode similar to constant-plane scanning AFM. The tip of the AFM lever is made magnetic and the tip is scanned in a constant plane *above* the surface of the magnetic sample, where the topographic forces are negligible compared to the magnetic forces. The potential of the tip/sample system is

$$U = - \int_{\text{tip}} \mathbf{M}_{\text{tip}}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) d\mathbf{r}, \quad (2.2)$$

where the volume integral is over the tip, $\mathbf{M}_{\text{tip}}$ is the tip magnetization, and $\mathbf{B}$ is the stray field from the sample. A truly massive effort has been put forth by many groups to quantitatively calculate the MFM contrast mechanism for varying $\mathbf{M}_{\text{tip}}$ models. [7] [8] [9] (See [9] for an extensive reference list.) Almost all of the work I present in this dissertation is derived from mostly qualitative

MFM measurements, to some degree because it is rather difficult to extract quantitative information without a careful calibration of $\mathbf{M}_{\text{tip}}(\mathbf{r})$, but primarily because it is simply not necessary in many cases; the contrast variations within an MFM image or series of MFM images will generally tell a complete story as long as certain precautions (detailed in a case-by-case basis in later chapters) are in place. With this in mind we take the first of many approximations, the dipole approximation. [10] Assuming that the main contribution to $\mathbf{M}_{\text{tip}}(\mathbf{r})$ is the dipole moment, $\mathbf{m}$, Eqn. 2.2 simplifies to

$$U = -\mathbf{m} \cdot \mathbf{B}. \quad (2.3)$$

The force is then

$$\mathbf{F} = -\nabla U = \sum_{i=x,y,z} \frac{\partial}{\partial i} (m_x B_x + m_y B_y + m_z B_z) \hat{i}, \quad (2.4)$$

where $\hat{x}$ and $\hat{y}$ are the cartesian unit vectors in the sample plane and $\hat{z}$ is normal to the sample. Now we make two more assumptions:

1. That the lever is only sensitive to forces in the $\hat{z}$ direction (not true since the lever is generally tilted around 12° from the x - y plane) so that the only part of $\mathbf{F}$ which affects the lever is F_z .
2. That $\mathbf{m}$ is parallel to $\hat{z}$ so that $m_x = m_y = 0$ (clearly not true for a general $\mathbf{M}_{\text{tip}}(\mathbf{r})$, especially including the 12° lever tilt and the fact that the surface of the tip is generally not normal to the surface of the cantilever).

With these in place, Eqn. 2.4 goes to

$$\mathbf{F} = F_z \hat{z} = m_z \frac{\partial B_z}{\partial z} \hat{z}. \quad (2.5)$$

In this MFM imaging mode, forces cause a pseudo-static deflection of the cantilever that is proportional to the field gradient $\frac{\partial B_z}{\partial z}$ at the tip position (taking the dipole approximation). For a nice demonstration of this technique, see [11].

2.2 Magnetic Force (Gradient) Microscopy

For many reasons, today most MFM is performed using a different scanning mode than that described in section 2.1. The cantilever is driven near resonance and can be modeled as a damped, driven simple harmonic oscillator with free resonant frequency f_0 . Dürig provides two methods for calculating the response of the lever to a general sample interaction. [12] The first, simpler method is to consider the case in which the oscillation amplitude of the lever is small compared to variations in the interaction force gradient above the sample surface. The lever feels an effective softening or stiffening due to the force gradient and the resonant frequency under the influence of the sample is given by

$$f = f_0 \left(1 - \frac{F'_z}{k} \right)^{\frac{1}{2}}, \quad (2.6)$$

with $F'_z = \frac{\partial F_z}{\partial z}$. Now we assume that $F'_z \ll k$,² Taylor expand Eqn. 2.6, and set negligible terms to zero. We end up with an expression for the frequency shift $\Delta f = f - f_0$:

$$\frac{\Delta f}{f_0} = -\frac{1}{2k} F'_z, \quad (2.7)$$

and plugging in F_z from Eqn. 2.5 we get

$$\frac{\Delta f}{f_0} = -\frac{m_z}{2k} \frac{\partial^2 B_z}{\partial z^2}. \quad (2.8)$$

Dürig also gives a method for calculating Δf for the case that the oscillation amplitude of the lever is large compared to variations in the interaction force gradient above the sample surface [12], but this is beyond the scope of this dissertation. We use lever oscillation amplitudes A around 50 nm, and considering that magnetic forces are relatively long-ranged, we feel safe in using the small amplitude approximation, especially since we do not try to extract quantitative information from the MFM images.

²This condition is always true for the data presented in this dissertation. F'_z is generally measured to be in the range of 10^{-6} to 10^{-3} N/m and k for the levers we use runs from 0.1 to 5 N/m.

Chapter 3

MFM Design and Operation Details¹

Since the first demonstration by Martin and Wickramasinghe, [13] MFM has improved continuously in terms of resolution, reliability, and ease of use, all while adapting to more extreme environments. The MFM described in this chapter was designed by Alex de Lozanne and is based on a variable-temperature (VT)-MFM also built in his lab that has been productive [14] [15] [16] [17] [18] [19] and is still in use. The heart of the new instrument is a microfabricated piezoresistive cantilever sensor, and there are four substantial improvements: in situ lateral positioning of the cantilever tip over the sample, external optical access to aid in positioning, a longer probe in order to reach a superconducting magnet inside a standard dewar, and a better heatsink to allow the MFM to reach lower temperatures. I describe these and other main features of this instrument.

3.1 Cantilever

Piezoresistive cantilevers (piezolevers) incorporate a doped Si layer that undergoes resistance changes proportional to lever deflection changes. [20]

¹Part of this chapter was submitted for publication in *Rev. Sci. Inst.* on 09/29/05.

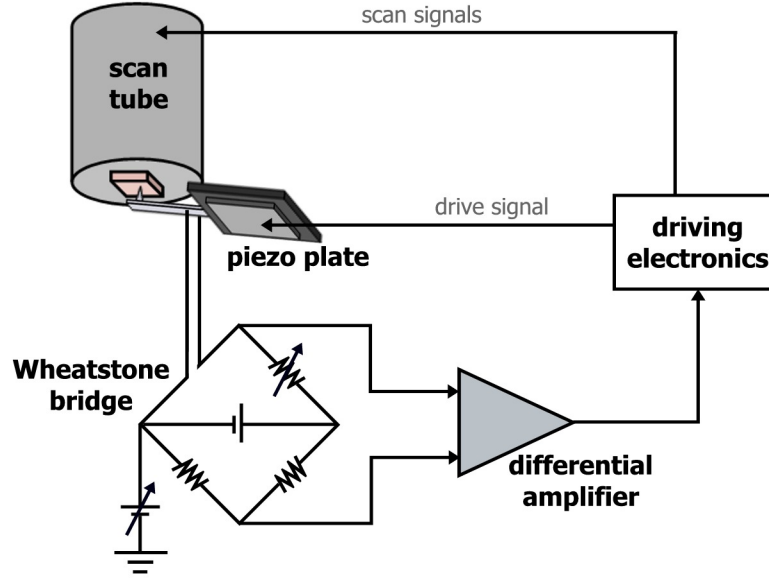


Figure 3.1: Diagram of the MFM.

This resistive layer serves as one arm of a dc-biased Wheatstone bridge that converts the resistance into a voltage signal (see Fig. 3.1). [21] This provides a simple way to read out lever deflection without the added complication of optical alignment and thermal drift issues that can accompany optical detection methods like fiber-optic interferometry. The disadvantages of choosing a piezoresistive deflection sensor are possible sample heating effects due to the power dissipated in the lever and dealing with noise levels elevated above the noise limit set by thermal excitation of the cantilever (empirically seen by Volodin et al. [22] and our group). We chose to use piezolevers over an optical detection scheme because many of the material systems we study have magnetic transitions that span wide ranges of temperatures. If we want to

track an area of the sample while varying the sample temperature from 250 K to 5 K and back, we can eliminate any possible optical misalignment induced by thermal drift by using piezolevers. Because the material systems of interest have relatively high magnetization values, the noise increase is rendered inconsequential. Sample heating may be an issue at the lowest temperatures, where heat capacities are lowest. We limit sample heating by placing an upper bound of 2 K on allowable cantilever heating through considerations of heat exchange gas pressures, heat conduction pathways, and piezolever power dissipation using the reasoning outlined by Giessibl et al. [21]

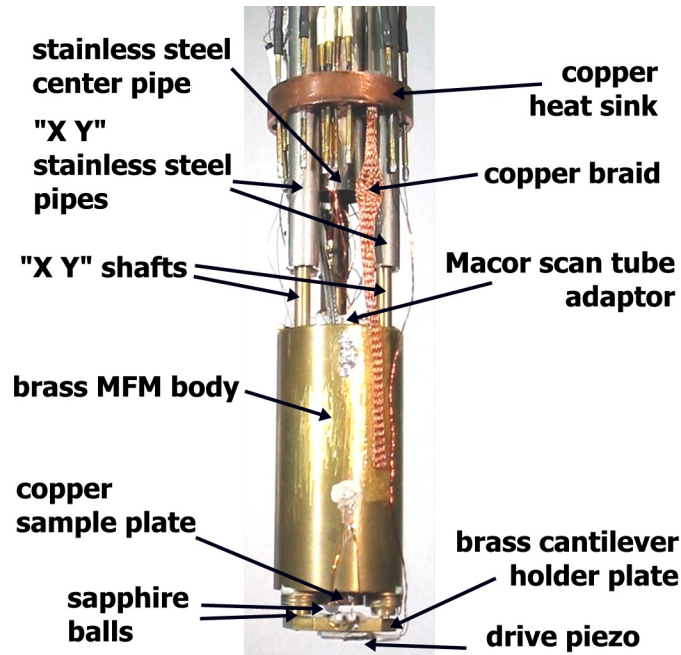


Figure 3.2: Details of the MFM probe.

Our first piezolevers were made by M. Tortonese at Park Scientific In-

struments. Recently we found a manufacturer of piezolevers in Japan (Seiko Instruments) with a distributor in the USA (KLA-Tencor). We have used both PRC400 and PRC120 cantilevers with spring constants of 2–4 N/m and 30–40 N/m, respectively. Since piezolevers are not currently available with a magnetic coating, we deposit Fe, Co, $\text{Co}_{85}\text{Cr}_{15}$, or $\text{Co}_{71}\text{Cr}_{17}\text{Pt}_{12}$ on the lever and integrated tip by evaporation or by sputtering, taking care to avoid shorting the piezoresistor embedded in the lever. The cantilever chip is fixed, tip pointing upward, to a brass cantilever holder plate with silver paint or epoxy. This plate is held against the bottom of the instrument, as shown in Fig. 3.2, has a hole cut in the center for optical access to the tip/sample region, and is thermally linked to the brass MFM body with a copper wire (0.32 mm diameter). A driving piezo plate is attached to the cantilever holder plate and serves to excite the resonance of the cantilever.

3.2 Scanner

We use the same tube scanner as in the previous design, a PZT-5H tube with four external electrodes and one internal electrode, 51 mm long, with outer diameter (OD) of 6.35 mm and wall thickness of 0.51 mm (Staveley Sensors). The maximum range of this scanner (± 200 V applied to outer electrodes) is approximately 160 μm at 293 K, 50 μm at 77 K, and 30 μm at 4.2 K. The scan tube fits inside a hole in the cylindrical brass MFM body and is fixed at the top with a Macor adapter (Fig. 3.2). The sample is mounted with the surface facing down on a copper sample stage attached to the bottom

of the scan tube just past the end of the MFM body. A Cernox temperature sensor (LakeShore) and a heater resistor are mounted on opposite sides of the sample stage. The copper sample stage is thermally linked to the MFM body with a copper wire (0.16 mm diameter). The MFM has four leads that can be used to connect to the sample to measure bulk resistivity or resistance of a patterned device in situ as a function of temperature and applied magnetic field.

3.3 Positioner

The x - y - z positioner is based on the traditional kinematic three-point mount: one ball fits into a cone on the cantilever holder plate, the second ball fits into a V-shaped groove, and the third ball presses against a flat surface. We chose sapphire for the balls and the flat surface due to its high rigidity and low friction with the aim of reliable, nonhysteretic motion. The third ball is driven by a 10-80 screw, which provides a very smooth approach mechanism in the $\hat{z}$ direction. The 10-80 screw is driven by a dedicated rotary manipulator at the top of the probe, coupled by a thin stainless steel pipe.

The novel aspect of this design is that it provides quasi- x - y positioning in a very compact design by mounting the first two balls mentioned above in an off-center position on rotating shafts, as shown in Fig. 3.3. When the first shaft is rotated, the first ball, which fits into a cone on the cantilever holder plate, makes this cone rotate in a circle about this shaft while the second ball slides along the V-shaped groove, as depicted by Fig. 3.3(c,d). For small rotations,

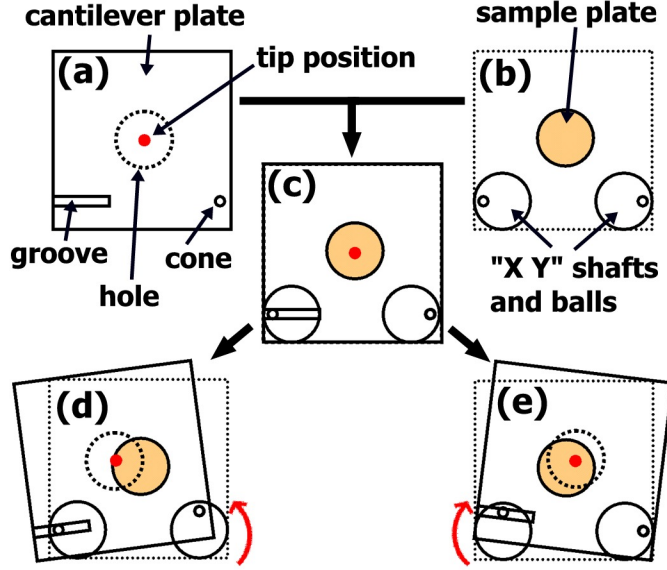


Figure 3.3: Schematic (looking along the probe axis from below) of (a) cantilever holder plate and lateral offset mechanism relative to (b) sample plate. (c) Cantilever plate superimposed on sample plate and “ x - y ” shafts and balls. (d) Cantilever plate offset after 90° rotation of rightmost shaft in (c). (e) Cantilever plate offset after 90° rotation of leftmost shaft in (c).

this makes the tip of the cantilever travel in an arc over the sample. When the second shaft is rotated, as in Fig. 3.3(c,e), the second ball slides inside the V-shaped groove, causing the cantilever holder plate to pivot about the first ball. The balls are offset by 0.76 mm from the center of the shafts, providing a maximum travel of 1.5 mm. However, the maximum range extends into a highly nonlinear regime, so the practical range is limited to several hundred microns. When the shafts for “ x ” and “ y ” are positioned as in Fig. 3.3(d), the quasi-linear portion of the motion is also quasi-orthogonal. We use quotes for “ x ” and “ y ” to emphasize the fact that these two axes are neither linear nor

orthogonal over long distances.

The shafts for “ x ” and “ y ” are rotated by thin stainless steel pipes that extend up to the top of the probe, where the head of a socket head screw is mounted on each pipe. The details of how these pipes couple to the rotating shafts on the MFM body are discussed in the next section. A single rotary manipulator attached to the top of the probe with a bellows drives a ball-head Allen key to engage and rotate either the “ x ” or “ y ” motion. Having separate, dedicated rotary manipulators for “ x ” and “ y ” would be more convenient although it would add to the cost and weight of the probe.

3.4 Support

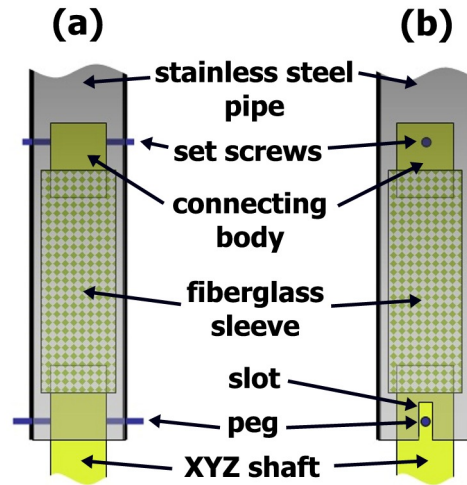


Figure 3.4: Peg and slot rotational coupling from an x - y - z pipe to an x - y - z shaft. (a) is rotated 90° with respect to (b).

The MFM body is supported by the equilateral arrangement of the

three thin pipes (6.35 mm OD, 0.15 mm wall, stainless steel) that provide rotary motion for x , y , and z positioning. To reduce vibrational coupling, the weight of the MFM body is supported by a short piece of fiberglass sleeve material on each shaft, while the torque is transmitted using a “peg and slot” arrangement, as shown in Figure 3.4. The three thin pipes are held in place, but allowed to rotate, by a copper heat sink above the MFM body and a similar aluminum circular plate at the top of the probe. The copper heatsink and aluminum plate are connected by a thin central pipe (11.1 mm OD, 0.15 mm wall, stainless steel) that provides rigidity for the probe as a whole. The aluminum plate at the top of the probe is free to slide up and down to accommodate differential thermal contraction, and the weight of the whole probe (or optional springs) provide the necessary force to press the copper heatsink against a copper sheath at the bottom of the pipe housing (described in the following section).

3.5 Chamber

The top of the probe has a small chamber made from a standard four-way cross with 70 mm flanges. The top flange connects to the two rotary manipulators mentioned above, while one side flange has a 20 pin feedthrough for electrical leads and the other side flange connects to a valve and pumping system. The bottom flange connects to the pipe housing for the instrument. The pipe housing is a standard stainless steel tube (31.8 mm OD, 0.71 mm wall). The pipe housing is removed every time a tip or sample is replaced.

While this is not as convenient as having a small canister attached at the bottom, it has the reliability and long life of a seal that remains at room temperature at the top of the probe.

In order to improve the thermal conductivity to the bath, the bottom of the pipe housing was machined to remove 0.33 mm from the inner wall, and a copper sheath (31.0 mm OD, 0.76 mm wall, 101 mm long) was press-fit into it. The copper heatsink presses against the top of this copper sheath and is thermally linked to the MFM body with a copper braid for better heat transfer from the MFM to the bath.

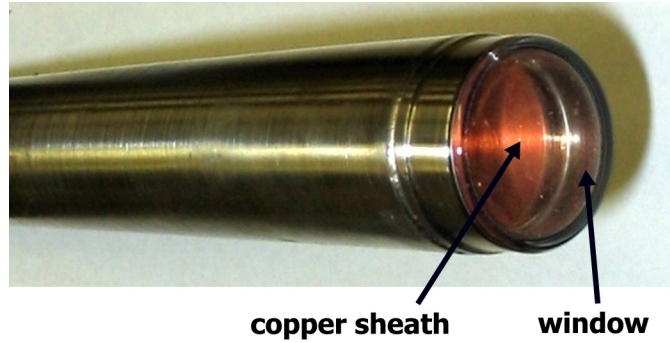


Figure 3.5: MFM pipe with integrated window. The copper sheath is visible behind the window.

The window at the bottom of the pipe housing (see Fig. 3.5) is an important feature of this design. We started with a standard glass viewport mounted on a standard NW25 flange (Model KVP-100 from MDC vacuum). The tapered portion of the NW25 flange was carefully machined away in order to match the 31.8 mm OD of the pipe housing and a short instep was machined

for alignment purposes. It was then welded at the bottom of the pipe housing. The differential thermal contraction between the glass window and the stainless steel body is taken up by a thin Kovar sleeve. Nevertheless, approximately half a year of thermal cyclings produced a small crack that started on one side of the glass window and propagated to the opposite side over approximately one more year. Surprisingly, the crack did not produce a measurable leak until it crossed the complete window, but fortunately it was possible to seal it with varnish (Kurt J. Lesker KL-5 leak sealant). We believe that this crack was initially due to a manufacturing defect, or some shock during machining or handling. An identical pipe and window has been thermally cycled from 77 K to room temperature roughly 100 times with no cracks thus far.

3.6 Electronics

We drive the scanner and acquire imaging data with a Nanoscope IIIa controller (Veeco-Digital Instruments). The lever deflection signal from the Wheatstone bridge is differentially amplified by a Stanford Research Systems SRS 560 Preamplifier (see Fig. 3.1). For MFM operation we use the frequency modulation technique [23], both with the commercial “Extender” available for the Nanoscope controller or with a digital phase lock loop (EasyPLL from Nanosurf). The latter required homemade electronics to interface with the Nanoscope controller. The homemade electronics consist mainly of a phase shifter to choose the phase setpoint for the phase lock loop and an rms-to-dc converter and comparator to generate the feedback signal for amplitude

modulated scans. Albrecht et al. showed that the minimum detectable force gradient using the frequency modulation technique is

$$\delta F'_{\min} = \sqrt{\frac{4 k k_B T B}{w_0 Q A^2}}, \quad (3.1)$$

where $w_0/(2\pi) = f_0$, Q is the quality factor of the lever, k_B is Boltzmann's constant, T is the temperature, and B is the measurement bandwidth. [23]

We operate the MFM in one of two modes, depending on the surface roughness of the sample. For flatter samples we generally use constant-plane scanning, recording the resonant frequency shift of the cantilever while scanning a plane aligned to and lifted off the sample surface. For rougher samples this scanning mode would result in a large average tip/sample distance and large variations in the tip/sample distance. Therefore, for rougher samples we generally use an interleaved scan mode, lift mode, whereby one line of topography (AFM) is acquired in frequency-modulated tapping mode (constant amplitude scanning) and then one line of MFM data is acquired by retracing the same topography at a certain lift height above the sample (while recording the resonant frequency shift of the cantilever). The interleaving of the topographic and magnetic images assures that they are spatially correlated, even when thermal drift is present. To null any electrostatic interaction between the tip and sample, the tip potential can be adjusted by changing the potential of the whole Wheatstone bridge (see Fig. 3.1).

There are at least three main reasons why this driven, frequency modulated MFM mode is preferable to the quasi-static mode described in section

2.1:

1. Deflection sensor spectral noise is generally higher at lower frequencies. A signal in the kHz regime (resonant frequencies are in this range) is significantly less noisy than a signal in the dc to few hundred Hz range.
2. We can take advantage of the high Q in vacuum to decrease $\delta F'_{\min}$.
3. Switching between topography and MFM acquisition during lift mode is very simple to implement, allowing rougher samples to be scanned with a small, constant tip/sample separation.

3.7 Optical Alignment of Tip and Sample

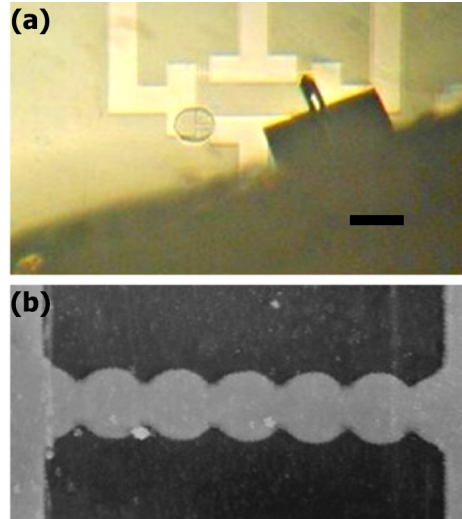


Figure 3.6: Lateral alignment of tip and patterned sample. (a) Optical image of patterned magnetic film and cantilever (scale bar $200\ \mu\text{m}$). (b) AFM image of patterned region ($55 \times 25\ \mu\text{m}^2$, 80 nm greyscale).

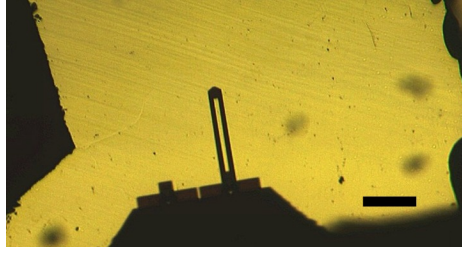


Figure 3.7: Optical image of $\text{La}_{1/4}\text{Pr}_{3/8}\text{Ca}_{3/8}\text{MnO}_3$ single crystal and cantilever (scale bar $200\ \mu\text{m}$).

Figure 3.6(a) shows an optical image of the tip/sample region after lateral alignment acquired through the window by a low resolution (640×480) USB web cam attached to an optical microscope. The cantilever and the patterned area of the sample are clearly visible (sample courtesy of Neil Mathur, Cambridge University). Figure 3.6(b) shows the corresponding AFM image of the patterned area. While this web cam is perfectly sufficient for this purpose, more recently we have obtained a high-resolution (1280×1024) CCD camera (uEye, USB2 interface) with better optics (Navitar and Mitutoyo) that allows us to align the cantilever tip with a particular portion of the sample, even for unpatterned samples. This is possible by finding particular defects or features that have been observed in other high-resolution optical microscopes or in a scanning electron microscope. An example is shown in Figure 3.7. Both cameras are able to record videos of the scanning motion.

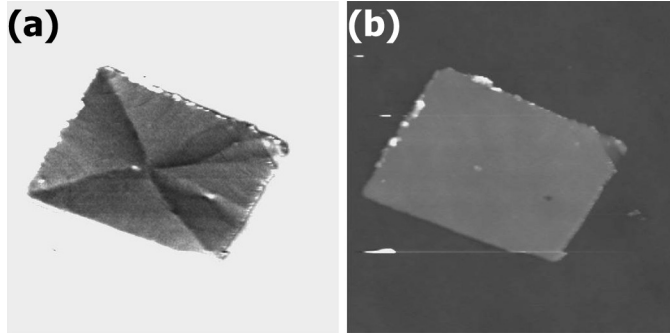


Figure 3.8: (a) MFM (1.5 Hz greyscale) and (b) AFM images of 40 nm thick, $12 \times 8 \mu\text{m}^2$ patterned permalloy element taken at 293 K. Cantilever parameters: tip coating 40 nm Fe / 1 nm Cr, $k = 3 \text{ N/m}$. Imaging parameters: lift mode, lift height 100 nm, $f_0 = 43.37 \text{ kHz}$, $Q = 4000$, $A = 52 \text{ nm}$, $B = 256 \text{ Hz}$, scan rate $20 \mu\text{m/s}$, measured force gradient noise $1.4 \times 10^{-5} \text{ N/m}$.

3.8 Experimental Results

The performance of the instrument as an MFM/AFM at room temperature is shown in Figure 3.8, where the cantilever was aligned with a patterned rectangular permalloy film on a silicon substrate and the data was taken in vacuum at room temperature. Patterned permalloy films generally form closure domains with magnetization in-plane. The apparent width and magnitude of the MFM contrast change at domain walls can serve as a calibration for both the lateral resolution and the remanent moment of low-moment² MFM tips.

The performance of the instrument as an MFM/AFM at low temperature and applied field is shown in Figure 3.9, taken at the tip/sample position

²Higher moment MFM tips can modify the domains structure in these films since the coercive field for permalloy is rather low.

shown optically in Fig. 3.7 on a polished single crystalline $\text{La}_{1/4}\text{Pr}_{3/8}\text{Ca}_{3/8}\text{MnO}_3$ sample (courtesy of S.-W. Cheong, Rutgers University). The MFM probe is inserted into an 8 T superconducting magnet dewar. The $15 \times 15 \mu\text{m}^2$ images are two frames of a temperature-dependent movie taken at a field of 1 T. Fig. 3.9(a) and (b) are the MFM and AFM images at 176 K. Fig. 3.9(c) and (d) are the MFM and AFM images at 7.4 K. Below about 220 K, this material is a phase-separated mixture of ferromagnetic (darker) and nonmagnetic (brighter) phases that evolve with changes in temperature and field. These images illustrate the ability of the MFM to explore a wide range of phase space while scanning the same region of a sample. Tip/sample lateral drift is typically several μm from 5 K to 293 K, well within the range of the scan tube. It is also possible to perform field sweeps at a constant temperature with even lower lateral drift. These results will be discussed in detail in Chapter 6.

We typically find that the MFM operates with force gradient noise about an order of magnitude greater than the thermally imposed minimum. [23] For instance, in Figure 3.9(a) the measured sensitivity is 1.1×10^{-5} N/m while the thermal limit is at 8.6×10^{-7} N/m. This discrepancy is not an issue when scanning samples with large magnetization. The noise can be reduced by either increasing the dc bias across the Wheatstone bridge at the expense of greater sample heating or by cooling the bridge resistors to lower their Johnson noise contribution. Volodin et al. were able to lower the force gradient noise in an MFM based on piezolevers by oscillating the lever at higher flexural modes. [22]

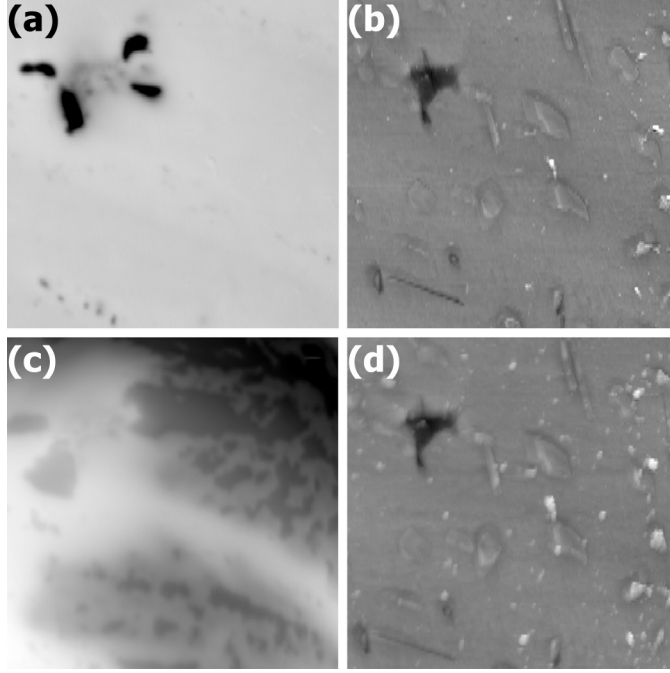


Figure 3.9: (a) MFM (6.5 Hz greyscale) and (b) AFM (50 nm greyscale) images of $\text{La}_{1/4}\text{Pr}_{3/8}\text{Ca}_{3/8}\text{MnO}_3$ single crystal at the position seen in Fig. 3.7 taken at 176 K in a 1 T field. (c) MFM (175 Hz greyscale) and (d) AFM (50 nm greyscale) images at same position taken at 7.4 K in a 1 T field. Cantilever parameters: tip coating 25 nm $\text{Co}_{85}\text{Cr}_{15}$, $k = 3$ N/m. Global imaging parameters: lift mode, lift height 50 nm, scan size $15 \times 15 \mu\text{m}^2$, $Q = 3000$, $A = 55$ nm, $B = 153$ Hz, scan rate $6 \mu\text{m/s}$. Imaging parameters for (a) and (b): $f_0 = 36.16$ kHz, cantilever $T = 60$ K, measured force gradient noise 1.1×10^{-5} N/m. Imaging parameters for (c) and (d): $f_0 = 36.25$ kHz, cantilever $T = 7.4$ K, measured force gradient noise 8.3×10^{-6} N/m.

Chapter 4

Introduction to Manganite Physics

For some materials (and fabricated devices), the resistance $R(B)$ changes with the application of a magnetic field, B . The ratio $\frac{R(B)-R(0)}{R(B)}$ is aptly termed the magnetoresistance (MR). In the vast majority of systems, the MR is small, say 5% or less, even for fields of order 1 T. By exploiting the interaction of currents with ferromagnetic layers spaced by nonmagnetic layers or coupled antiferromagnetically, devices can be produced with $\text{MR} \approx -200\%$. This effect, discovered in 1988, was dubbed the giant magnetoresistive (GMR) effect [24] [25], and today GMR heads are used in computers to sense stray fields from the magnetic platters in hard disks and read out data.

4.1 CMR effect

In 1994, Jin et al. presented data from $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin films showing a MR of $-127\,000\%$ at 77 K in a 6 T field. [26] This unprecedented behavior was immediately christened the colossal magnetoresistive (CMR) effect. Many manganites of the form $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R is a trivalent rare-earth ion and A is a divalent dopant) exhibit the CMR effect for a wide doping range around $x = 1/3$. They have the perovskite structure, shown in Fig. 4.1 (but

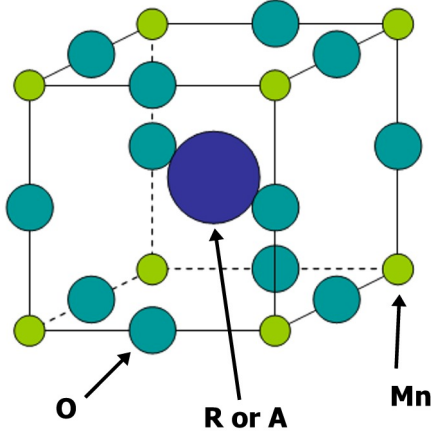


Figure 4.1: The perovskite structure.

generally are the slightly distorted $Pnma$ structure). Generally speaking, these materials show an insulator–metal transition from a high–temperature insulating phase to a low–temperature metallic phase marked by a peak at T_P in the resistivity versus temperature curve. This phase transition is accompanied by a magnetic transition from a high–temperature nonferromagnetic phase to a low–temperature ferromagnetic (FM) phase at the Curie temperature, T_C .

The doping of A^{2+} ions in R^{3+} sites results in a mixed Mn^{3+}/Mn^{4+} valence, with $4 - x$ Mn d -shell electrons per Mn. The cubic crystal environment splits the 5 $3d$ orbitals into a t_{2g} triplet and an e_g doublet, as shown schematically in Fig. 4.2. Hund’s rule coupling aligns all these valence electrons. So, 3 electrons go to the t_{2g} triplet, creating a core spin, and the remaining $1 - x$ electron can be in the e_g doublet at a Mn site if its spin is aligned with the core spin.

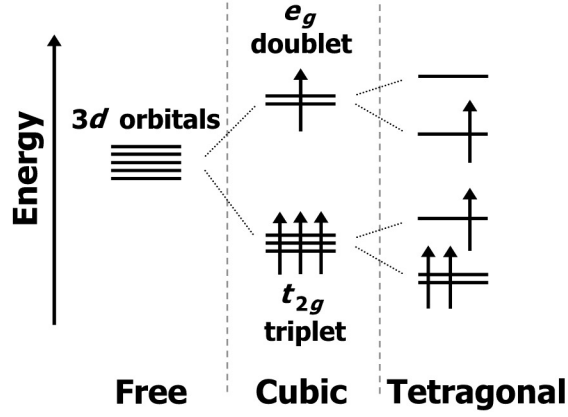


Figure 4.2: Crystal field splitting of Mn d -orbitals. From the left: free Mn ion, Mn in cubic crystal environment, Mn in tetragonal crystal environment.

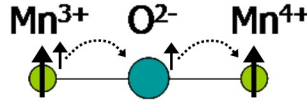


Figure 4.3: Double exchange mechanism. Core spins represented by big arrows, hopping electrons by small arrows.

The phase transition at $T_P \approx T_C$ is interpreted partly in terms of Zener's double exchange theory. [27] Specializing it to this case, it outlines the simultaneous transfer of 2 electrons, 1 from an O^{2-} to the e_g orbital of an adjacent Mn^{4+} site and another from the e_g orbital of an adjacent Mn^{3+} to the O^{2-} (see Fig. 4.3). Because of the strong on-site Hunds coupling, this process happens more often when the Mn moments are parallel (FM state). In turn, the hopping electrons promote FM order because they tend to preserve their spin direction. An applied magnetic field tends to align Mn core spins against

thermal fluctuation, shifting both T_P and T_C to higher temperatures, providing a qualitative explanation for the CMR effect. However, the double exchange mechanism alone is not sufficient to describe the high-temperature transport properties and to quantitatively explain the magnitude of the CMR effect. Therefore, some other mechanisms such as electron-phonon coupling [28] due to local Jahn-Teller distortions at the Mn^{3+} sites and orbital ordering effects [29] must be considered. The degeneracy of the e_g doublet can be broken by a tetragonal distortion of the cubic crystal environment, thereby lowering the total energy of a Mn^{3+} site and the surrounding O^{2-} ions, as seen in the right-most part of Fig. 4.2. These driving mechanisms conspire to produce a very complex phase diagram as a function of x . [28] Many of the neighboring phases have similar ground state energies; consequently, the phase boundaries can be readily displaced by perturbations such as the application of a magnetic field [30], of mechanical or structural pressure [31], or by chemical pressure arising from substitutions of rare earth ions with differing ionic radii. [32] This latter possibility is interesting because it has been shown to result in large-scale electronic phase separation and to produce strongly hysteretic behavior in the transport properties.

Chapter 5

An MFM Study of the Magnetic Structure in a CMR Film around the Insulator–Metal Transition¹

There is growing experimental and theoretical evidence that the doped manganites are electronically inhomogeneous and that phase separation is common in these materials. [33] [34] Uehara et al. used electron microscopy to study the $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ system. [32] Changes in the Pr doping (y) lead to changes in the internal chemical pressure of the system due to the slight ionic size difference between La^{3+} and Pr^{3+} . They found that at low temperatures, below T_P , the system is electronically phase separated into a micrometer-scale mixture of Jahn–Teller–distorted, insulating regions and nondistorted, metallic FM domains, although they could not characterize the local magnetic properties of these domains. They explained the CMR effect by percolative transport through the FM domains; a magnetic field aligns the magnetizations of FM domains that are dispersed in a configuration that is near the percolation threshold. By the double exchange mechanism, electrons can now move easily along these FM pathways and the resistance is lowered.

¹Part of this chapter was published in ref. [19]

In this chapter I present the direct observation of the formation of these percolative networks as the sample is cooled, and their disappearance upon warming. Upon cooling, the isolated FM domains in thin films of $\text{La}_{1/3}\text{Pr}_{1/3}\text{Ca}_{1/3}\text{MnO}_3$ start to grow and merge at the metal–insulator transition temperature T_{P1} , leading to a steep drop in resistivity, and continue to grow far below T_{P1} . In contrast, upon warming, the FM domain size remains unchanged until near the transition temperature. The jump in the resistivity results from the decrease in the average magnetization. The FM domains almost disappear at a temperature T_{P2} (higher than T_{P1}), showing a local magnetic hysteresis in agreement with the resistivity hysteresis. Even well above T_{P2} , some FM domains with higher transition temperatures are observed, indicating magnetic inhomogeneity. These results give a few clues as to the origin of the CMR in these materials and include a few surprising findings: the FM domains continue to grow and change at temperatures well below T_{P1} during cooling and upon warming they still exist at temperatures above T_{P2} .

5.1 Experimental Setup

All of the data presented in this Chapter was taken using the lift mode technique described in Section 3.6 with a lift height of 100 nm. We used noncontact Piezolevers² with resonant frequencies around 110 kHz. The lever is made sensitive to magnetic forces by depositing a 50 nm Fe film on one side of the tip and magnetizing it along its axis.

²Park Scientific Instruments (now Digital Instruments), Santa Barbara, CA.

The domain patterns of CMR films with different easy axes have different shapes. [35] MFM images of our sample indicate an in-plane easy axis. Because the MFM is sensitive to force gradients perpendicular to the sample, in order to see clearly the domains instead of the domain walls, a perpendicular magnetic field is used to partially align the magnetization of the FM domains out-of-plane. In the case of the cooling sequence, the MFM tip itself provides this cooling field. For warming images we first cooled the sample across T_{P1} to a low temperature in a 2.5 mT magnetic field perpendicularly applied to the whole sample, then turned off the field before scanning during warming. The thermal drift of the tip position relative to the sample was compensated for during image acquisition with lateral offsets of the scan piezo and adjustments of the coarse approach mechanism to follow the same area of the sample. This data was not taken with the MFM described in Chapter 3, but with a previously built MFM. [14] In this MFM, a change in the direction of the coarse approach mechanism causes an unpredictable change in the lateral position of the sample, preventing us from scanning the same area of the sample when changing from cooling to warming. The temperature change rate was roughly 0.1 K/minute during scanning.

The films were grown on NdGaO₃ (NGO) (110) substrates by pulsed laser deposition to a thickness of 60 nm. They were grown in an oxygen atmosphere of 400 mTorr at a rate of about 1 Å/second at a substrate temperature of 820 °C. The temperature dependence of the resistivity of the film (Fig. 5.1) shows that on cooling from room temperature, the resistivity grad-

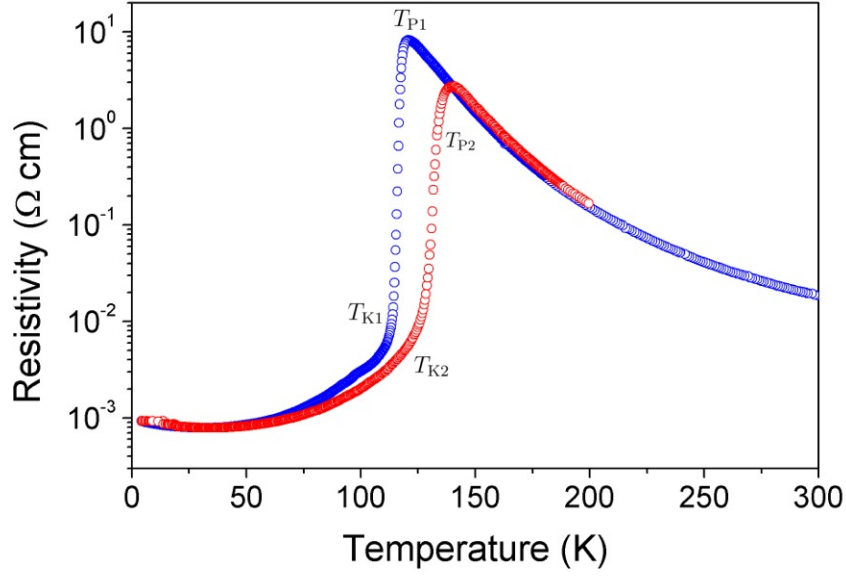


Figure 5.1: The temperature-dependent resistivity of the $\text{La}_{1/3}\text{Pr}_{1/3}\text{Ca}_{1/3}\text{MnO}_3$ thin film over a thermal cycle. The blue series corresponds to cooling, the red series to warming.

ually increases, attaining a maximum at $T_{P1} = 120$ K. This is followed by a steep resistivity drop to the knee temperature $T_{K1} = 114$ K, and then slow changes to 4.2 K. On warming, the resistivity follows the cooling curve at first, then deviates to lower values. After an abrupt jump beginning at the warming knee temperature $T_{K2} = 128$ K, the resistivity reaches a maximum at $T_{P2} = 140$ K, and finally coincides with the cooling curve at high temperature. T_{P2} is 20 K higher than T_{P1} , showing a pronounced hysteresis typical of a first-order phase transition. The resistivity values are similar to those of single crystals of these compounds [36], but the transition widths are much narrower for the thin films (about 8 to 9 K). Unfortunately, the magnetization of these 60 nm

films on NGO is difficult to measure due to the paramagnetic substrate [37].

5.2 Temperature Dependent MFM data

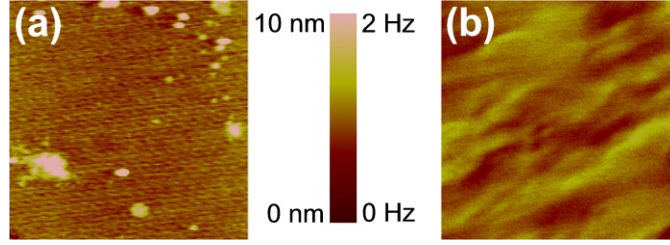


Figure 5.2: (a) Topography image and (b) the corresponding MFM image recorded on the same area ($7.5 \times 7.5 \mu\text{m}^2$) of the sample at 120 K during warming.

Figure 5.2 shows a simultaneously acquired topographic image and MFM image well below T_{P2} . Comparison of the two images indicates that the main features in the MFM image have no counterparts in the topography image. The features in the MFM image are due to the nonuniform magnetic field distribution above the sample surface; they are produced by FM domains of differing magnetization in the sample.

The MFM images taken during cooling at one area and warming at another area are displayed in Fig. 5.3³. During the cooling process the MFM

³I emphasize that all of the sets of cooling and warming images obtained on different areas of the sample with different cantilevers show qualitatively the same temperature-dependent evolution of FM domains. As described in the text, during cooling from room temperature to T_{P1} , all the images are uniform, and from low temperature to T_{K2} during warming, both the size and the contrast of the images are nearly unchanged. To maintain the consistency between the resistivity hysteresis and the micromagnetic hysteresis, we have

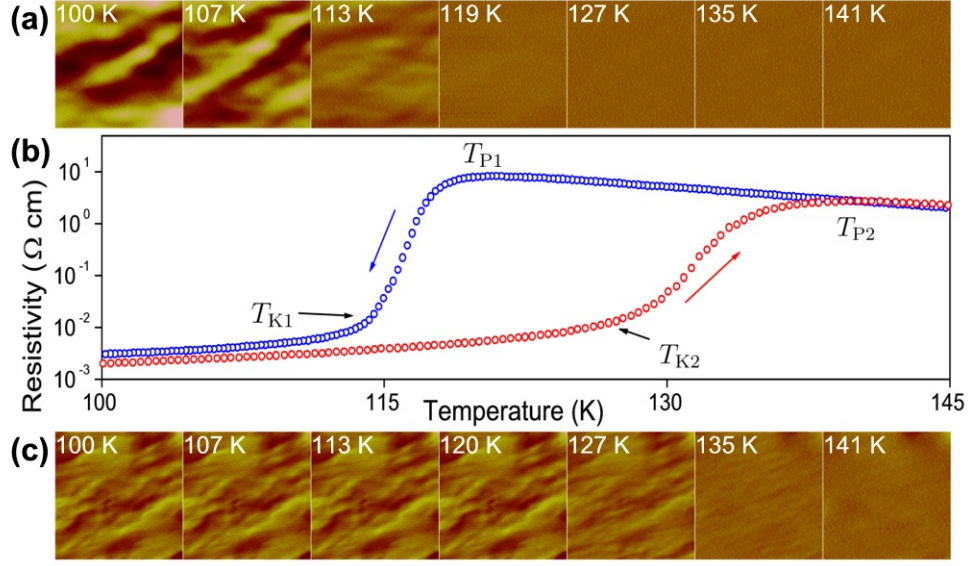


Figure 5.3: The temperature-dependent MFM image sequence (a) for cooling and (c) for warming, and the resistivity (b) of the $\text{La}_{1/3}\text{Pr}_{1/3}\text{Ca}_{1/3}\text{MnO}_3$ thin film over a thermal cycle. The blue series corresponds to cooling, the red series to warming. The center of each image is aligned horizontally with the temperature scale from (b) at the time of image capture. Scanned areas are $6 \times 6 \mu\text{m}^2$ for all cooling images and $7.5 \times 7.5 \mu\text{m}^2$ for all warming images. All cooling images were taken at one area of the sample, all warming images were taken at another area.

images are nearly uniform above T_{P1} . Just below T_{P1} , the contrast starts to appear. The contrast of the sequence is gradually enhanced with decreasing temperature, indicating that the magnetization of the FM domains becomes increasingly stronger. The features gradually merge into continuous pathways in the MFM field of view. Just past T_{K1} the percolation of the contrast features,

simply reproduced the three highest temperature images in Fig. 5.3(a) and the three lowest temperature images in Fig. 5.3(c).

and therefore the FM domains, is clearly seen. When the temperature is decreased further, although the change in the resistivity is smaller, the contrast of the image continues to increase and the FM domains merge and enlarge, which is an unexpected result.

However, during warming below T_{K2} , both the contrast and the size of the FM regions are nearly unchanged. Above T_{K2} , although the size of the FM regions is constant, the contrast rapidly decreases. At T_{P2} the contrast almost completely disappears. The hysteresis in the local magnetic microstructure is consistent with the resistivity hysteresis and qualitatively consistent with the magnetization measurement on polycrystalline samples with similar composition. [38]

5.3 Discussion

The FM domains in the warming images have a much smaller size than the cooling images at the same temperatures below T_{K1} . This difference is likely due to the way in which the sample is cooled. The tip of the MFM vibrates above the sample surface at the resonant frequency of the lever, 110 KHz, contacting the sample at the lowest point of each oscillation. At this contact point, the magnetic field applied by the tip is large (10 to 100 mT). [39] Roughly, as the tip is scanned, a strong periodic magnetic pulse with a frequency of 110 KHz is scanned over the sample. We believe that upon cooling, although this scanning, localized magnetic pulse may not change the relative FM volume fraction in the film [40], it may assist in driving the motion

of the domain walls, leading to the formation of FM domains with a large characteristic length scale. On the other hand, the warming images were obtained after the sample was cooled to the lowest temperature in a magnetic field of 2.5 mT. This was done to coarsely simulate the effect of the scanning tip during cooling and to begin the warming scans with a sample state similar to the end of the cooling scans. During this cooling process, the tip is far away from the sample. This cooling field may not be strong enough to move the domain walls. When scanning during warming, the domain walls are strongly pinned. As a result, the MFM image sequence does not show many changes. As T_{P2} is approached, the average magnetization decreases, which results in a rise in the resistivity (Fig. 5.3(b)). [41] Our observations indicate that during cooling, the percolation of the FM domains causes the steep resistivity drop, whereas during warming, the FM conductive paths remain until near T_{P2} , but the decrease in the average magnetization leads to the jump in resistivity. This may explain why the knee in the resistivity is sharper during cooling than during warming.

Even well above T_{P2} , there is still a slight but discernable contrast in some areas. We propose that this is due to the magnetic inhomogeneity above T_P that is frequently observed in similar CMR materials. [42] [43] [44] Due to the constraining effect of the substrate, some effects observed in bulk samples may be suppressed or different for these thin films. [36] This might account for the sharper transitions in the thin films and the narrower hysteresis regions. This implies that the temperature-dependent magnetic microstructure in thin

films is modified due to the effect of the substrate.

These results confirm that the local magnetic structure is correlated with the hysteresis in resistivity and magnetization versus temperature and that growth and merging of FM domains is a key part of the insulator–metal transition in prototypical CMR manganites.

Chapter 6

An MFM Study of the Magnetic Structure in a CMR Single Crystal around a Glass-Like Transition¹

We chose to investigate the issue of electronic phase separation in CMR manganites more thoroughly in a similar sample to the one discussed in Chapter 5. As previously stated, the $\text{La}_{1-x-y}\text{Pr}_y\text{Ca}_x\text{MnO}_3$ ($x = 3/8$) system exhibits large scale phase separation for a wide region of parameter (y , temperature, field, etc.) space. [32] Recent experimental and theoretical efforts increasingly emphasize the importance of μm -scale phase separation around field and temperature induced transitions, where percolation is key in understanding the CMR effect, especially in manganites with low Curie temperatures (T_C). [32] [44] [19] It is suspected that this large scale phase separation is caused by the accommodation strain arising from the lattice mismatch between the FM metallic phase (pseudo-cubic) and the charge-ordered (CO) insulating phase (orthorhombic). [45] This point of view is supported by both experiments and simulations. [36] [46] Therefore, it is important to understand the thermodynamics of this strain-stabilized phase separation, yet little has

¹Part of this chapter was submitted for publication in *Science* on 10/11/05.

been done.

6.1 Chemical Pressure and Glassy Behavior

$\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$ (LPCMO) is a model system for investigating the role of chemical pressure and accommodation strain on a phase-separated state. With the Ca doping held constant at $3/8$, the carrier concentration is fixed, and changes in the Pr doping (y) lead to changes in the internal chemical pressure of the system due to the slight ionic size difference between La^{3+} and Pr^{3+} . Both the phase separation balance and length scale depend strongly on y . [32] Recently, Sharma et al. presented evidence supporting the classification of LPCMO ($y = 0.41$) as a “strain glass” at low temperature [47], where hysteretic behavior is found in isothermal field sweeps. [48] The glass transition is buried inside this large hysteresis so that it is hard to detect. Similar isothermal hysteretic behavior has been observed in various manganites, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, etc. as well. [49] This similarity suggests that they might share the same glass-like state at low temperature.

The glassy behavior seen in phase-separated manganites is reminiscent of the well-studied spin glass transition in Mn-doped Cu [50], which is signified by the bifurcation of the zero-field-cooled (ZFC) and field-cooled (FC) susceptibility $\chi(T)$ below T_G . A wide class of heavily disordered ferromagnets have been termed “cluster glasses” because they tend to show similar behavior in $\chi(T)$. [51] It has been speculated that the magnetization of FM clusters freezes in a random fashion below the cluster glass transition and the mag-

netization of each cluster acts like an individual spin in a spin glass. Since many phase-separated manganites also exhibit typical cluster glass behavior, [47] [48] it may be natural to assume that the cluster glass picture is a suitable description of the phase-separated manganites. The local magnetic configuration of the glassy state in both disordered ferromagnets and phase-separated manganites has never been studied on the scale of individual clusters, despite the fact that “cluster glass” is commonly used to describe these material systems. In particular, no real-space imaging technique has been used to study the cluster glass transition. Here, we succeed in imaging a possible cluster glass transition in LPCMO ($y = 3/8$). Upon warming through T_G , the “cluster glass” picture predicts only that each frozen FM cluster magnetization would be free to rotate, implying no significant change in FM volume fraction. In contrast, we found that the FM volume fraction increases drastically, reflecting the collective nature of the transition. Our results further confirm that the mesoscopic scale phase separation found in LPCMO using electron microscopy is representative of the bulk. [32] It would be interesting to extend our study to other compounds showing similar behavior.

In this Chapter, I describe the results of variable-temperature magnetic force microscope (VT-MFM) studies on single crystal LPCMO ($y = 3/8$), a composition in which μm -scale phase separation has been observed. [32] After ZFC from room temperature to below T_G , the MFM images demonstrate that the frozen glass state prevents the formation of new FM regions, even with the application of a 1 T field. As the temperature approaches T_G during

fieldwarming (FW), more and more nonmagnetic regions are converted to FM domains along orthorhombic twin boundaries. Near and just above T_G , the FM regions grow into an extensive stripe-like pattern, correlating with the sharp rise in bulk magnetization and the sharp decrease of resistivity. As the temperature is increased further, the phase pattern remains relatively constant with some fraction of the sample remaining nonmagnetic (presumably the CO phase, which is antiferromagnetic below 180 K [48]) over a wide range of temperature, agreeing with magnetization and resistivity data. In contrast to this ZFC-FW strain-glass-like transition, during the FC-FW process the local phase configuration and therefore magnetization and resistivity are relatively static. It is found that the FM domains, once formed, persist even after the field is turned off, indicating that the FM and CO phases have similar free energies over this temperature range, a conclusion which is in agreement with previous work. [32]

6.2 Experimental Setup

Single crystal samples of LPCMO ($y = 3/8$) were synthesized in an optical floating zone furnace. One sample was mechanically cut, polished with 0.1 μm paper with water, and annealed in an O_2 atmosphere at 1000 $^\circ\text{C}$ for 10 hours. The original sample was cleaved into two pieces, one for SQUID measurements and one for VT-MFM and transport measurements. All the MFM images were taken after inserting the MFM into a superconducting magnet before scanning. All of the data presented in this Chapter was taken

with the MFM described in Chapter 3 using the lift mode technique described in Section 3.6 at a lift height of 50 nm. We used PRC400 Piezolevers² with resonant frequencies around 35 kHz. The lever is made sensitive to magnetic forces by depositing a 25 nm thick layer of $\text{Co}_{85}\text{Cr}_{15}$ on the tip and magnetizing it along its axis³. Two copper wires were attached to the sample by silver paint for two-probe resistance measurements taken simultaneously with MFM data.

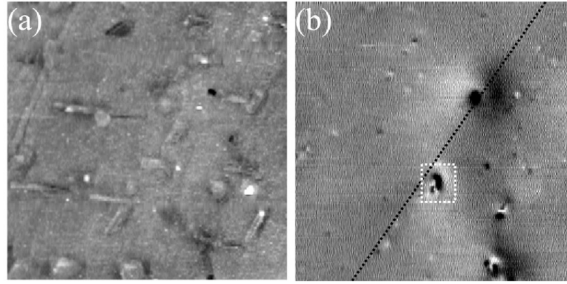


Figure 6.1: Zero field topography (a) and MFM (b) images of the same area ($15 \times 15 \mu\text{m}^2$) taken at 6 K. The gray scale is 30 nm for (a) and 150 mHz for (b). In the MFM image several small FM droplets can be seen embedded in the nonmagnetic CO background. The FM droplets range in size from roughly 100 nm to 1 μm . While the majority of the smaller FM droplets are single domain, some of the larger FM droplets break up into multi-domain states (one is highlighted by the white dashed box). The magnetization of each FM droplet is oriented randomly. The FM droplets tend to form lines parallel to twin boundaries (one is marked by the black dashed line).

Fig. 6.1 shows a typical topographic image and the corresponding MFM image at 6 K after ZFC. The in situ resistance is too large to measure at 6 K. The MFM contrast mechanism is set forth in Section 2.2 and in [23] and

²KLA-Tencor

³ $H_C \approx 50$ mT.

[7]. Briefly, an attractive (repulsive) force on the MFM tip that decays with distance from the sample gives rise to a negative (positive) frequency shift. In the ZFC case of Fig. 6.1(b), the local moments of each of the FM regions have a relatively random orientation so that there are both attractive (dark) and repulsive (bright) places, depending on the specific magnetization direction in each region. Fig. 6.1(b) shows several small FM droplets ranging in size from about 100 nm to 1 μ m scattered in a nonmagnetic matrix, presumably the CO phase. There is a tendency for some of these FM droplets to line up parallel to a nearby twin boundary⁴, although many have no correlation with surface defects and twin boundaries. The magnetization of the FM droplets is oriented randomly. Some big droplets have a multi-domain structure to lower their magnetostatic energy.

The small fraction of the FM phase agrees well with the in situ resistance measurement and ex situ SQUID and resistivity measurements. Thinking in broad terms of the “cluster-glass” picture outlined above, we might interpret this state to be the frozen, low temperature state. The seemingly uniform size of the smallest, randomly distributed FM droplets implies that the droplets are intrinsic to the sample and that the balance of the two competing phases which determines the size of each droplet does not depend on location.

⁴At and below room temperature, LPCMO possesses an orthorhombic distortion away from cubic symmetry and forms so-called orthorhombic twins. The optical anisotropy of the orthorhombic lattice can be used to identify different twin domains and the twin boundaries. By matching landmarks in optical images and large area topographic scans, we are able to align the MFM images with polarized optical images.

6.3 Temperature Dependent MFM data

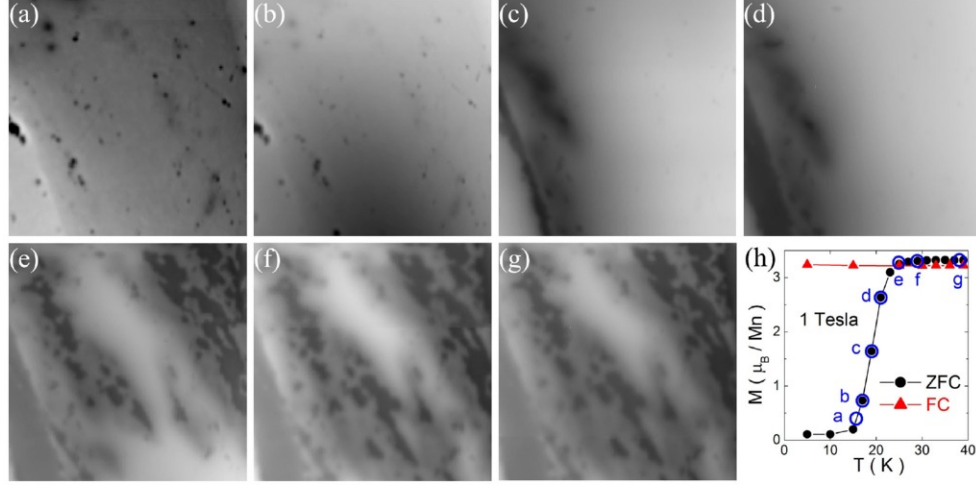


Figure 6.2: MFM images of one area of the sample ($10 \times 10 \mu\text{m}^2$) during ZFC–FW (1 T) around T_G . The temperatures (gray scales) of the images are: (a) 16 K (12 Hz), (b) 17 K (30 Hz), (c) 19.4 K (172 Hz), (d) 21 K (217 Hz), (e) 25.5 K (172 Hz), (f) 30 K (120 Hz) and (g) 38 K (141 Hz). (h) Temperature dependence of the magnetization (M vs. T) during FW. The glass transition occurs around $T_G \simeq 20$ K where the ZFC–FW curve rises sharply to approach the FC–FW curve. As T_G is approached and passed, MFM images show FM regions (dark) appearing and growing to form stripe-like structures parallel to twin boundaries. As the temperature is increased further, the MFM images remain relatively unchanged with some fraction of the sample remaining nonmagnetic (the CO phase), agreeing with the plateau in (h).

At low temperature after ZFC, the CO phase persists unless a field larger than the CO melting field is applied. [48] [52] Fig. 6.2 shows a series of MFM images taken during FW in a 1 T field after ZFC. In a moderate magnetic field, e.g. 1 T, the magnetization of both the FM regions in the sample and the MFM tip are aligned with the external magnetic field. Therefore, the

only force between them is attractive; the darkest places in the MFM images correspond to regions with the highest effective moment, averaging over a volume beneath the surface. Images taken from 5 K to 16 K show no significant changes and are omitted from Fig. 6.2. Fig. 6.2(h) shows the temperature dependence of the magnetization of the sample in a 1 T field during FW after ZFC and FC. Comparing Fig. 6.2(a–g) with Fig. 6.2(h) we conclude that the bulk magnetization is a good measure of the volume fraction of the FM phase at 1 T. The ZFC data in Fig. 6.2(h) show a sharp rise in magnetization from 15 K to 25 K as MFM images confirm a significant increase in the FM fraction and the in situ resistance drops to a finite value. Some of the long length scale features in the MFM images are likely due to the formation of large FM regions well beneath the sample surface. The FM regions tend to grow into stripe-like structures during the transition. For this choice of field (1 T), some CO regions persist above T_G (bright color at the top-center of the frame in Fig. 6.2(e–g)).

In contrast to the MFM images taken during ZFC–FW near and below T_G , the FC–FW images from the same temperature range show that the local phase configuration is relatively static, agreeing with the magnetization data in Fig. 6.2(h). This history dependence provides evidence for a glassy state. [47] These FC–FW images will be presented elsewhere.

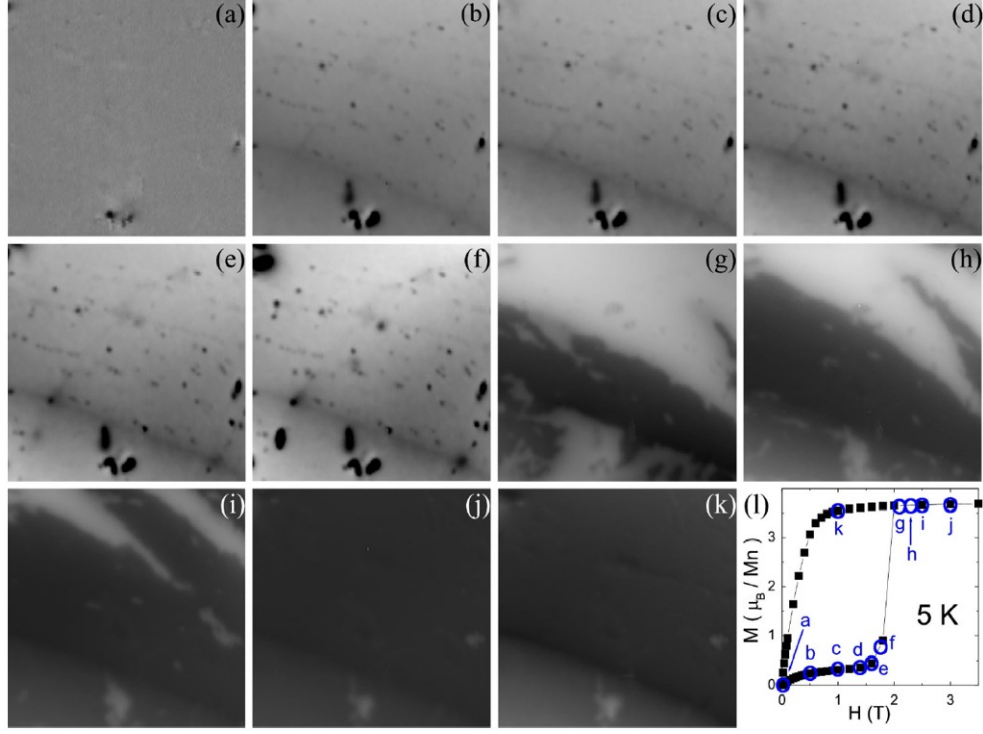


Figure 6.3: MFM images of one area of the sample ($15 \times 15 \mu\text{m}^2$) at various magnetic fields at 6.8 K after ZFC. The field values (gray scales) of the images are: (a) 0 T (2.3 Hz), (b) 0.5 T (8 Hz), (c) 1.0 T (8 Hz), (d) 1.4 T (8 Hz), (e) 1.6 T (8 Hz), (f) 1.75 T (8 Hz), (g) 2.1 T (150 Hz), (h) 2.3 T (150 Hz), (i) 2.5 T (150 Hz), (j) 3.0 T (150 Hz) and (k) 1.0 T (150 Hz). (l) Field dependence of the magnetization (M vs. H) at 5 K. The CO melting field is around 2 T. As the melting field is approached and passed, MFM images show FM regions (dark) appearing and growing at the expense of the CO phase (bright). FM regions form stripe-like structures parallel to twin boundaries. With the application of a 3 T field (j), all of the CO phase in the MFM image frame is converted to the FM phase, with the exception of a few small CO regions likely pinned by surface defects. As the field is lowered to 1 T (k), the sample stays magnetically saturated and (almost) fully FM, agreeing with the data in (l).

6.4 Field Dependent MFM data

In Fig. 6.3 we show a series of MFM images taken during an isothermal magnetic field sweep at 6.8 K after ZFC. During the initial upswing of the field, no significant increase of the FM fraction is seen below the CO melting field $H_M \simeq 2$ T. For fields above 0.5 T, the magnetization of all the FM droplets is aligned with the external field. This agrees with the small magnetic anisotropy and coercive field of three-dimensional manganites. [33] At H_M , the FM regions grow to stripe-like structures aligned parallel to the twin boundaries as the magnetization jumps up (Fig. 6.3(l)) and the sample resistance drops to a measurable value, as seen in Fig. 6.4. The CO phase persists in mesoscale stripe-like features at fields up to 2.5 T as shown in Fig. 6.3(i). The CO stripes disappear after a field increase to 3 T (Fig. 6.3(j))⁵. At this point the sample is fully FM, with the exception of a few small CO regions likely pinned by defects.

The sample now behaves like a conventional isotropic FM with a ~ 0.5 T saturation field; Fig. 6.3(k) is an MFM image taken at 1 T showing no changes in the FM state of the sample. Once the FM phase in LPCMO ($y = 3/8$) is developed either by melting the CO phase with a field above H_M or by warming the sample above T_G in a moderate field, it persists until the temperature approaches T_C , where the metal-to-insulator transition is observed.

⁵The fact that the bright color is swept out of the MFM images around H_M gives further credence to our identification of the bright color with the CO phase.

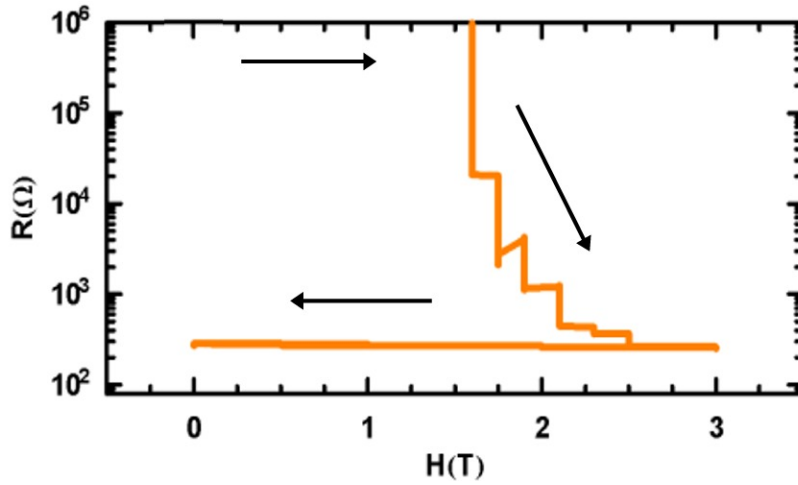


Figure 6.4: Two-probe resistance of the sample taken in situ during MFM scans from Fig. 6.3. The seemingly sharp steps in R are artifacts of sitting at a single value of H for ≈ 45 minutes as each MFM image is acquired and then sweeping H relatively quickly to the next value.

6.5 Discussion

One common feature in both the glass transition (Fig. 6.2) and the melting transition (Fig. 6.3) is that the FM domains form stripe-like features along orthorhombic twin boundaries where a large strain variation is expected (Fig. 6.5). Some FM droplets in the ZFC state also tend to line up along twin boundaries. These correlations demonstrate that the martensitic accommodation strain plays a crucial role in the evolution of μm -scale phase separation in manganites.

An emerging theme in the manganite community is that both competing phases and quenched disorder are needed to generate the CMR effect. [53] [54] [55] [56] [57] The CMR regime is also where glassy behavior is usually

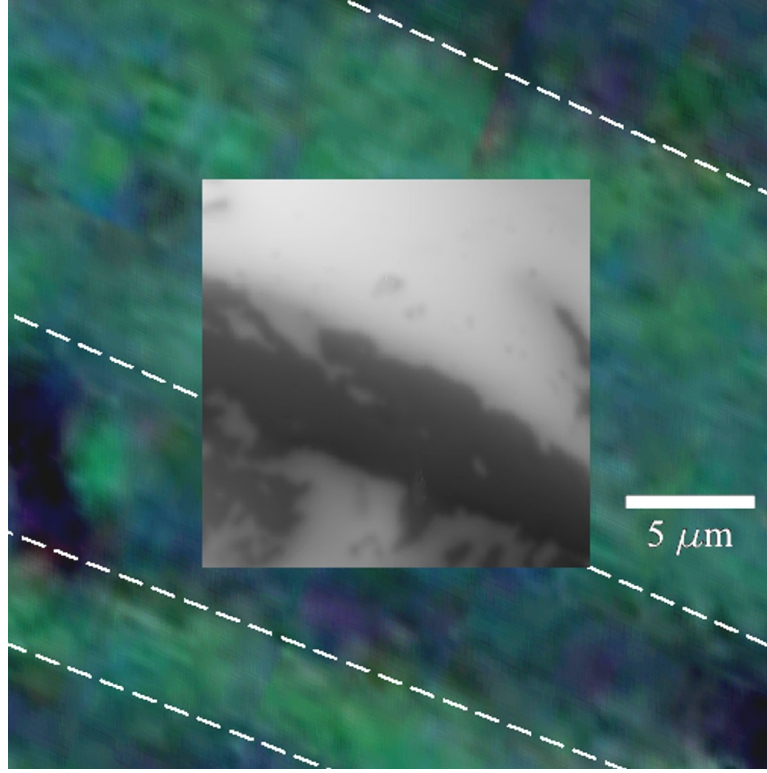


Figure 6.5: MFM image from Fig. 6.3(g) superimposed on a polarized optical microscope image from the surrounding region of the sample. Orthorhombic twin boundaries are highlighted by white dashed lines.

found. It is not clear whether manganites should be described as canonical cluster glasses or not, especially since there is no clear microscopic picture for conventional cluster glasses. In conventional cluster glasses the frustration arises from the competition of random magnetic couplings, while in manganites it comes from the competition of different phases. Regardless of the microscopic origin of frustration, the macroscopic properties of phase-separated manganites resemble those of conventional cluster glasses. If LPCMO can be

categorized as a type of cluster glass, our results provide a clear picture of the cluster glass transition on a local scale. In contrast to the commonly held view that only reorientation of the FM cluster magnetization happens at the cluster glass transition, we show a significant increase of the FM volume fraction, a result consistent with recent magnetization relaxation studies. [47] [58] Further microscopic investigations of both conventional cluster glass systems and CMR manganites will bring out the similarities and differences between them, helping to clarify the microscopic understanding of cluster glass systems. We might be able to answer the question: Are the CMR manganites a new class of cluster glasses? [59]

These results show that the phase-separated LPCMO system undergoes a collective phase transition into a glassy ground state as a result of the degeneracy of the FM and CO phases and inherent quenched disorder under the freezing influence of accommodation strain energy barriers. Mesoscopic scale phase separation is an intrinsic behavior of LPCMO and it may be universal across CMR manganites.

Chapter 7

Thin-Film Manganite Devices

Using the optical alignment procedure outlined in Chapter 3, we have studied the formation of magnetic domain walls in patterned thin-film manganite devices with the goal of measuring their transport properties.

7.1 Magnetic Domain Walls in Manganites

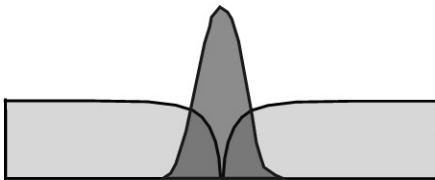


Figure 7.1: Order parameters across a magnetic domain wall in a manganite doped such that the FM and CO phases have similar energy. The magnetic order parameter is shaded light, the CO order parameter dark. Adapted from ref. [34].

In Chapters 4 and 5, I introduced the concept of phase coexistence in the CMR manganites. If we take a prototypical CMR manganite doped such that the ferromagnetic (FM) and charge-ordered (CO) phases have very similar free energy, then we can imagine that if the order parameter of the dominant phase is lowered then the other phase can form. [34] This idea is

illustrated in Fig. 7.1. In a normal magnet, the magnitude of the FM order parameter is nearly constant across a domain wall, but Fig. 7.1 illustrates the possibility that if the FM order is lowered at a domain wall, the CO phase may form a localized inclusion. Experimentally, we should be able to explore this possibility by looking at the resistance of domain walls, specifically looking for a high resistance state if the more insulating CO phase forms a break in the primarily FM, metallic sample.

Mathur et al. fabricated planar devices from $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ with the intention of measuring the domain wall resistance–area product from a well defined number of domain walls. [60] The domain wall resistance–area product was calculated from the device’s geometry and the resistance measurement. This value was compared to the value calculated under the assumption of no break in the FM order parameter, only from the decrease in electron bandwidth as magnetization rotates across the domain wall. The measured value of the resistance–area product turned out to be four orders of magnitude higher than the calculated value, supporting the idea of the inclusion of the insulating CO phase at magnetic domain walls.

We are using MFM to attempt to confirm the location and number of domain walls in these devices and characterize the nature of the phase separation at a domain wall. Figure 7.2 is an optical image showing the current pathway through the device and the shadow of the MFM cantilever (The device is just past the end of the cantilever). Figure 7.3 is a higher magnification image of the device, showing that it consists of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ patterned on

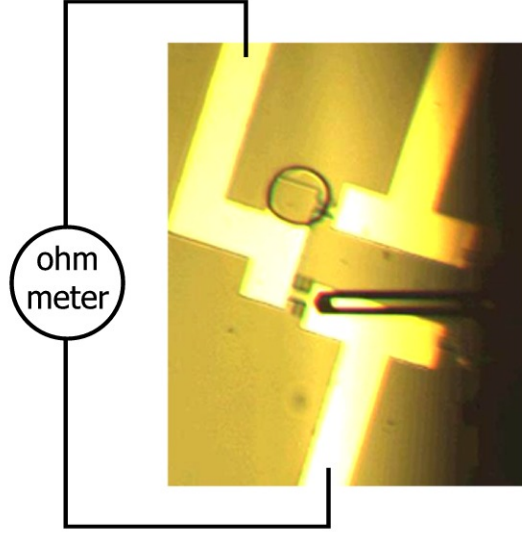


Figure 7.2: Optical image of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ domain wall device mounted inside the MFM.

an NdGaO_3 substrate with constrictions to pin domain walls and an additional array of Co magnets that serve to set a different switching field for the aligned $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ elements and the unaligned elements. The uniaxial magnetocrystalline anisotropy sets the easy axis of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ device. The external field is applied along the easy axis.

7.2 MFM and Transport data

Figure 7.4 shows two-probe field-dependent transport data of a similar device to the one shown in Fig. 7.3. The sharp downward jumps in resistance at about ± 10 mT are signatures of the disappearance of domain walls as the device moves from a multi-domain state to a saturated state.

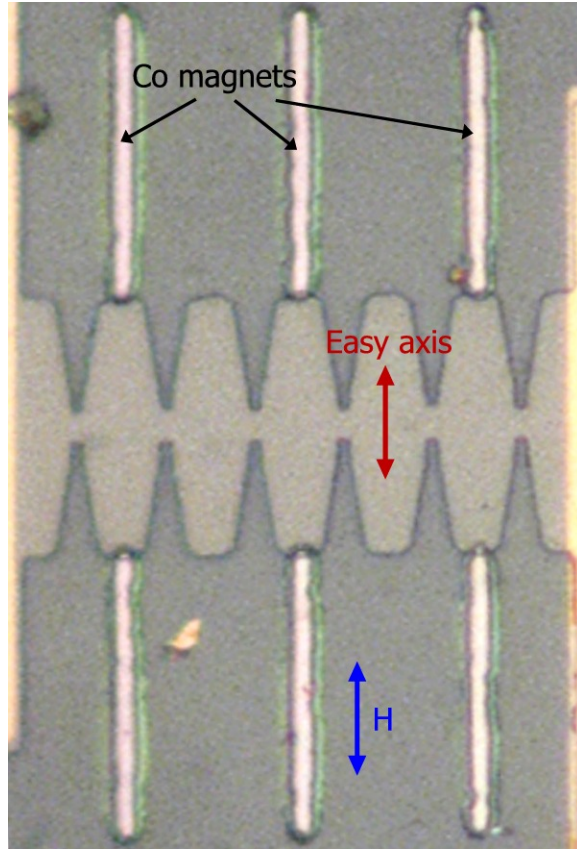


Figure 7.3: Optical image of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ domain wall device showing the adjacent Co magnets.

Figure 7.5(a)–(d) shows MFM images of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ device shown in Fig. 7.3. All of this data was taken at 77 K. We perform MFM scanning and take transport data simultaneously. Figure 7.5(e) shows the R–H data from this scanning run. The first thing to note is that the R–H data in Fig. 7.5(e) is qualitatively different from the ex situ data presented in Fig. 7.4. These differences seem to be explained by the presence of the scanning

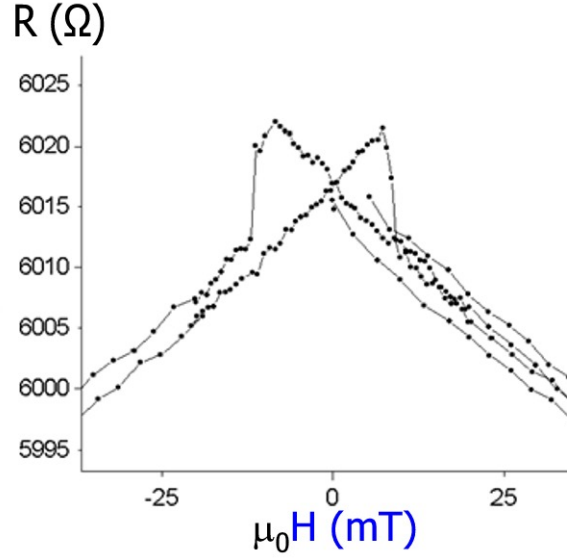


Figure 7.4: Ex situ transport data of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ domain wall device at 77 K.

MFM tip, accelerating the switching process.

Looking at the optical image in the top-right of Fig. 7.5, we see that the outside parts of the MFM image frame are the track elements that are adjacent to the Co magnets. Fig. 7.5(a) is taken at -2.1 mT after positive saturation and there are almost no changes in the MFM images over this entire field range (not shown). With the arrows, we show that we think the magnetization is still pointing in the positive H direction throughout the device. Thinking in terms of the build up of fictitious magnetic charge, the bright and dark contrast at the constrictions can be understood to arise from the large $\mathbf{M} \cdot \hat{\mathbf{n}}$ at the walls (edges) of the film.

Fig. 7.5(b) is taken at a more negative field, -6.6 mT. Here we can see

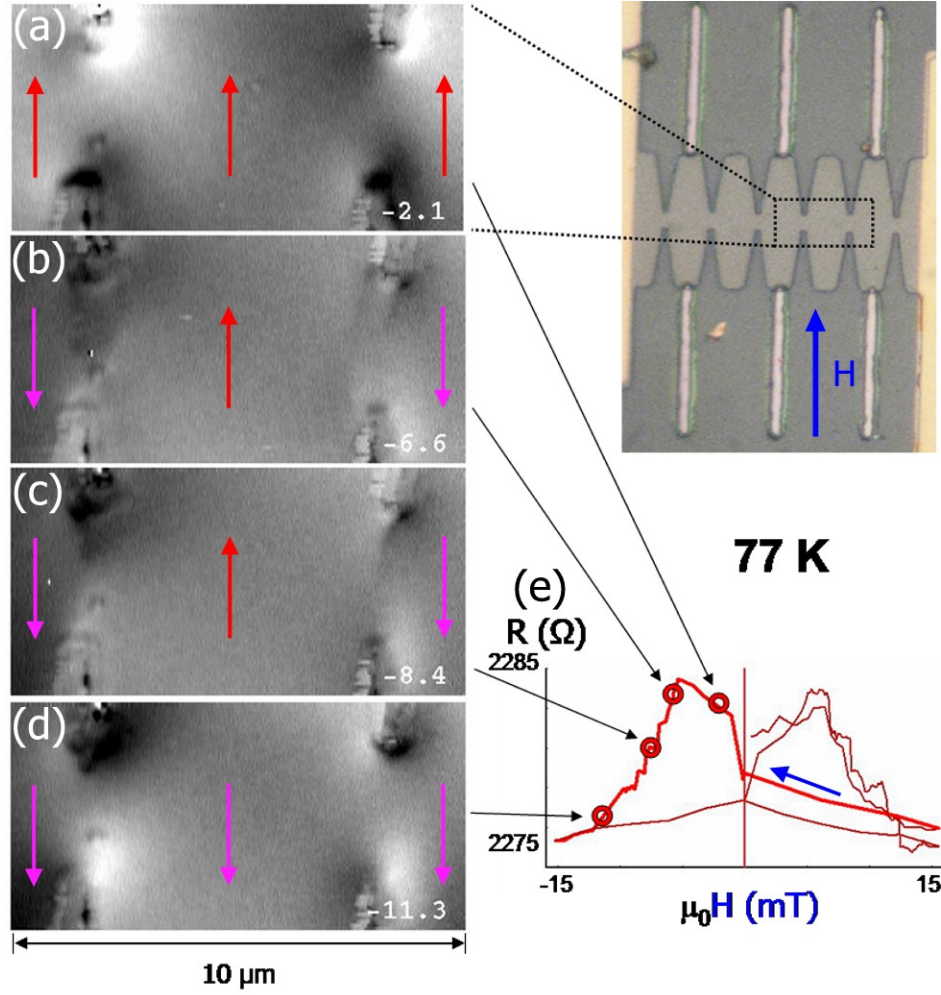


Figure 7.5: (a)–(d) MFM images and (e) in situ transport data of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ domain wall device at 77 K. The MFM images come from the region of the device boxed at the top-right of the Figure. Each MFM image is labeled with the field value in mT and the magnetization direction for each track element. The data is taken on lowering H from positive saturation.

some vertical line features cutting across the constrictions. Again, thinking in terms of fictitious magnetic charge, these features can be understood as arising from the divergence of the magnetization, $\nabla \cdot \mathbf{M}$, at domain walls. As the field is swept more negative, the domain walls move inward as negative magnetization becomes increasingly energetically favored (Fig. 7.5(c)). When the field is swept even more negative, to -11.3 mT (Fig. 7.5(d)) all the domain walls disappear and the track is saturated in the negative direction. Note that the MFM contrast is reversed relative to Fig. 7.5(a).

A close examination of the original, finely-spaced MFM images and transport data shows that there is a drop in resistance whenever a domain wall disappears. The resistance jumps are likely due to domain walls in the transport pathway. If so, the domain wall resistance–area product increase may be 4 or 5 orders of magnitude higher than expected. This suggests that the inclusion of the CO phase at domain walls may actually be taking place.

7.3 Questions

There are some issues with this project as it now stands. The R–H data certainly has some qualitative dependence on the presence or absence of the scanning MFM tip. The tip which was used for this data was coated with 25 nm of $\text{Co}_{85}\text{Cr}_{15}$. It is possible to reduce the effect of the tip on the sample by depositing a lower moment coating on the tip, either by reducing the thickness of the coating or by moving to a lower moment material altogether.

The MFM images do not show repeatable devices states, that is, the

configuration of the domain walls is not just a function of field history. This may be another artifact of the effect of the stray field of the MFM tip. It may be possible to design a more robust device through micromagnetic simulation.

7.4 Micromagnetic Simulation

Cursory simulation using the OOMMF¹ software package from NIST [61] supports the formation of domain walls at the device constrictions. Figure 7.6 shows the result of a simulation set up with a random initial magnetization that was allowed to relax to an energy minimum state, first at zero field (Fig. 7.6(a)), then at successively larger negative fields (Fig. 7.6(b)–(d)). Values for the exchange stiffness and anisotropy constant come from ref. [60]. The diagonal domain walls move outward as negative magnetization becomes more favored and get trapped vertically at the constrictions, bowing out more as the negative field is ramped up. This is shown in Figure 7.7.

The features cutting diagonally across the track in Fig. 7.6(a) are similar to features seen in MFM scans of the track taken in the constant-plane scanning mode described in Section 3.6. In this mode the tip does not come into contact with the sample, so the effect of the tip on the sample may be reduced. Fig. 7.8 compares an MFM image for a constant-plane scanning series with a zoom in of Fig. 7.6(a).

Missing from these simulations is the central postulate that we are

¹<http://math.nist.gov/oommf/>

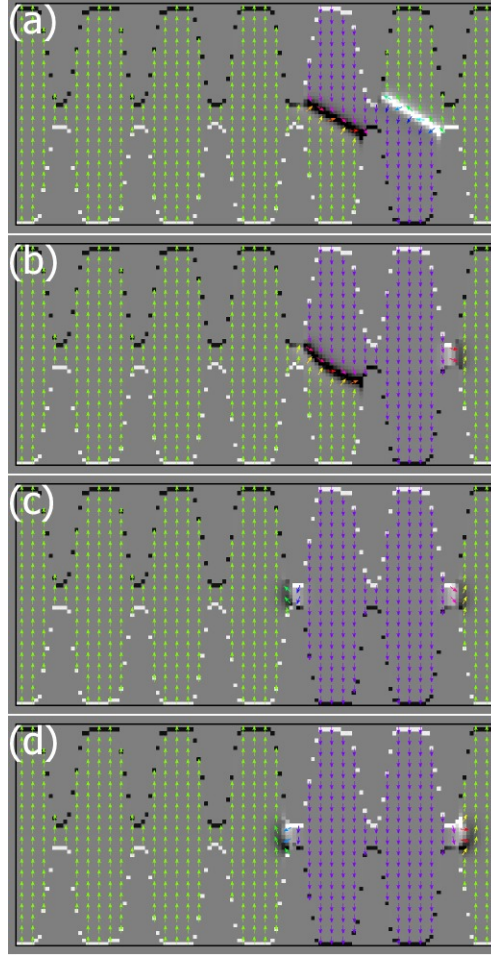


Figure 7.6: Micromagnetic simulation of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ device. (a) An initial random magnetization state was set up and allowed to relax in zero field to an energy minimum state. Magnetization direction is signified by the arrows. $\nabla \cdot \mathbf{M}$ is signified by the background greyscale. (b)–(d) Relaxed states after the application of increasing large negative fields. Simulation parameters: saturation magnetization 1.6×10^5 A/m, exchange stiffness 5×10^{-10} J/m, uniaxial ($\hat{\mathbf{y}}$) anisotropy constant 10^5 J/m³, image size 6.45×3 μm^2 , cell size $50 \times 50 \times 50$ nm³.

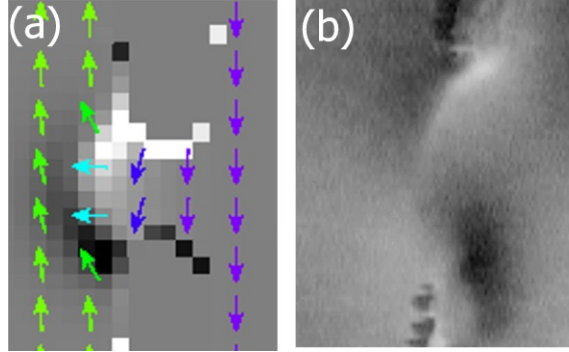


Figure 7.7: (a) Zoom-in of micromagnetic simulation result shown in Fig. 7.6(d) and (b) MFM image showing vertical domain wall. (MFM contrast inverted to match simulation contrast.)

trying to examine, that of an inclusion of the CO phase at a domain wall. Referring back to Fig. 7.1, we can see that the magnetization may really drop to near zero in the center of the domain wall. If this is so, then the Néel domain walls (magnetization rotates in-plane) seen in Figs. 7.6–7.8 may have a different structure in the real device. This idea is shown in Fig. 7.9. The magnitude of the magnetization drops at the center of the domain wall and the magnetization itself does not rotate away from $\hat{y}$. Anisotropy energy is lowered relative to the Néel wall geometry. Since $\nabla \cdot \mathbf{M} = 0$ across this domain wall, it may explain the empirical fact that there is a difficulty in seeing a vertical domain wall in the MFM images.

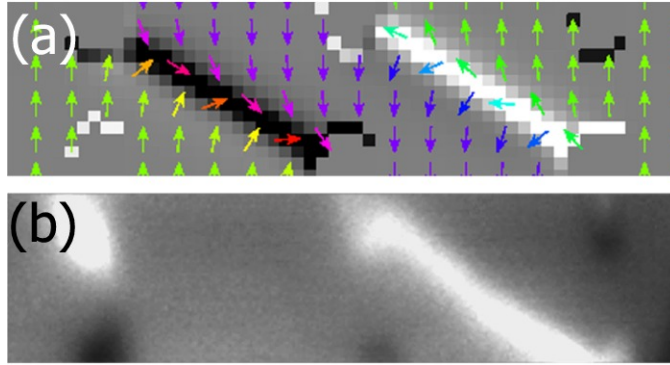


Figure 7.8: (a) Zoom-in of micromagnetic simulation result shown in Fig. 7.6(a) and (b) MFM image showing diagonal domain wall.

7.5 Future Direction

The micromagnetic simulations can include different materials (like the Co magnets) and can also be performed for different thicknesses of the Co and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ elements. It seems like the diagonal and vertical domain walls are both local energy minimum states. It may be possible to eliminate, for instance, the diagonal walls through further micromagnetic simulation and refinement of the device geometry. The inclusion of the CO phase at domain walls most likely changes the micromagnetic energy terms relative to a traditional Néel wall. Perhaps there is some way to incorporate this into the simulation.

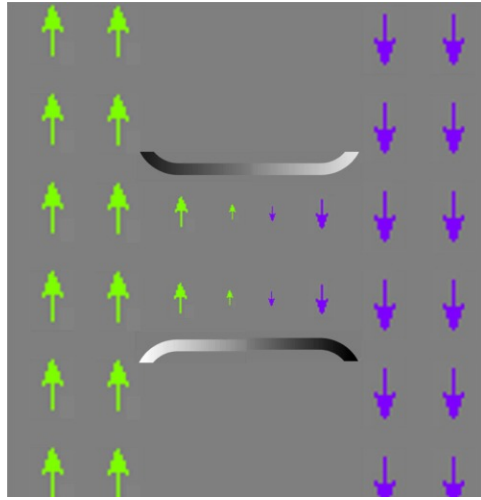


Figure 7.9: Vertical domain wall at a constriction with the inclusion of CO phase. Vectors represent magnitude and direction of magnetization. Note that at the domain wall itself, $\nabla \cdot \mathbf{M} = 0$.

Chapter 8

Electrostatic Force Microscopy

Since the piezoresistive cantilevers that we use for the MFM are weakly conductive from the doped resistive channel to the end of the tip¹, we can also perform electrostatic force microscopy (EFM) with an arbitrary bias applied to the tip. Even with the cantilever held at ground potential, induced charges can build up on the tip in the presence of electric fields and lead to attractive potentials.

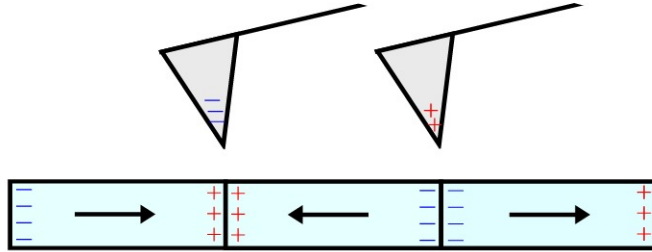


Figure 8.1: Electrostatic Force Microscopy on ferroelectric materials. A ferroelectric material breaks up into domains with different polarization directions (shown in-plane here). Charges build up at the domain boundaries and serve as the source of electric fields which induce an opposite polarization of the conducting tip.

¹This is an empirical observation, it may be partly due to the doping of the lever and/or the metal layer we deposit on the cantilever

For example, for an idealized ferroelectric material with polarization direction in the sample plane, static charges are present at the boundaries between domains of differing polarization direction (see Fig. 8.1). When the tip is above a domain boundary, the tip has an induced charge of opposite sign, leading to an attractive potential. Since the induced charge always opposes the polarity of the sample, the interaction is always attractive and according to Eqn. 2.6, the resonant frequency shift Δf of the cantilever is always negative.

8.1 Introduction to $\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3\text{:LuMnO}_3$

Park et al. found that doping Lu into the CMR manganite $\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3$ causes a chemical phase segregation into a mixture of orthorhombic, ferromagnetic, metallic $\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3$ (LSMO) and hexagonal, ferroelectric LuMnO_3 (LMO). [62] They studied issues of three-dimensional percolation in this mixture of metallic and insulating regions.

This material is a sort of multiferroic, albeit a phase-separated one, in that both ferromagnetism and ferroelectricity are present in the same sample. We studied a sample of $(\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3)_{0.2}(\text{LuMnO}_3)_{0.8}$ with the aim of examining the ferromagnetic domain structure in the LSMO, the ferroelectric domain structure in the LMO, and the possibility of interplay between the two. The sample was grown by the floating zone method, then cut and polished such that the c -axis of the crystal (the ferroelectric polarization axis) is in the scanning plane. Polarized optical microscopy can differentiate between the LSMO and LMO phases, and also LMO regions with differing c -axis orientation (see

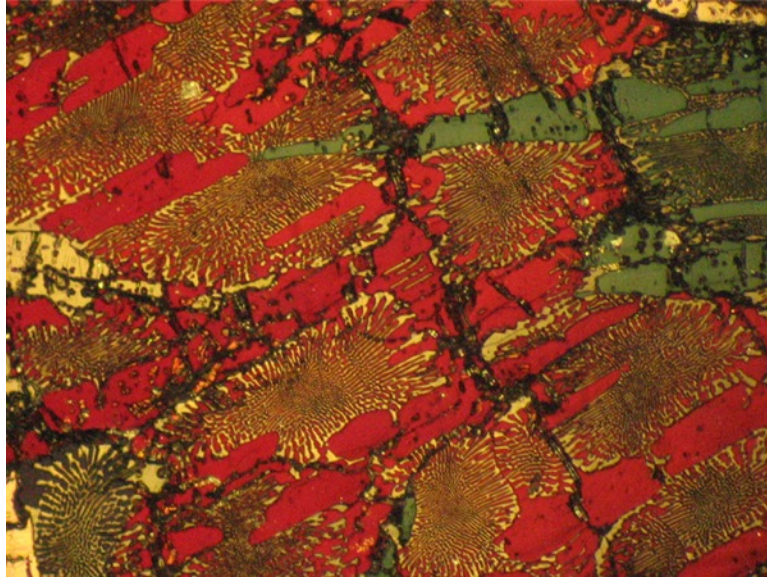


Figure 8.2: Polarized optical microscope image of $(\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3)_{0.2}(\text{LuMnO}_3)_{0.8}$ sample. The majority LuMnO_3 phase shows up as different colors based on the in-plane c -axis direction, while the minority $\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3$ phase has no optical anisotropy and shows up as the light color. Image size: $500 \times 300 \mu\text{m}^2$.

Fig. 8.2).

8.2 MFM/EFM Scans of $(\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3)_{0.2}(\text{LuMnO}_3)_{0.8}$

A room temperature MFM/EFM scan and zoom in is shown in Figure 8.3. The first thing to note is the presence of MFM contrast from the ferromagnetic domain structure in the LSMO regions (rougher, lower regions in the topography). This is highlighted in the zoom-in in Fig. 8.3(d). LSMO has a T_C of about 370 K. Also notable is the lack of EFM contrast in the LMO regions (the smoother regions in the topography), even though the ferroelectric

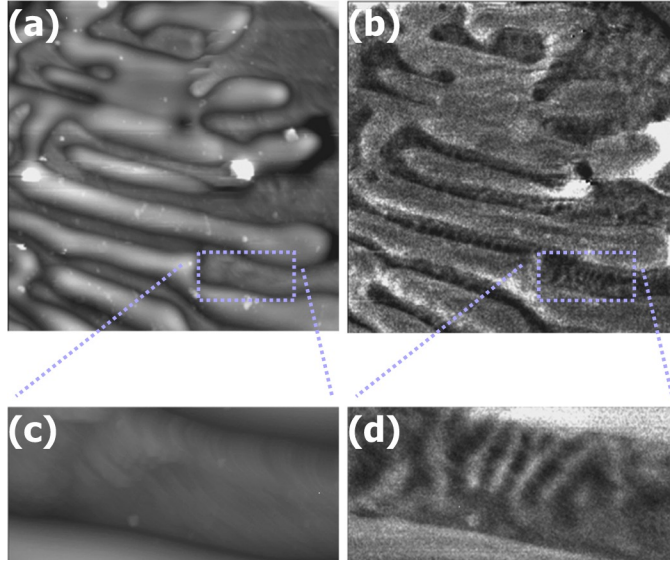


Figure 8.3: (a,c) Room temperature topography ($1\text{ }\mu\text{m}$ greyscale) and (b,d) MFM/EFM scans (1.5 Hz greyscale) of $(\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3)_{0.2}(\text{LuMnO}_3)_{0.8}$ sample. (a,b) image size: $40\times 40\text{ }\mu\text{m}^2$.

ordering temperature, T_{CFE} , is 900 K.

An EFM scan of the sample taken at 77 K is shown in Fig. 8.4(b). For this set of scans we used a tip with moment $\mathbf{m}$ very nearly zero. This is why there is no MFM related contrast from the LSMO regions of the sample. Fig. 8.4(b) shows very strong contrast in the LMO regions arising from ferroelectric domains. With the assumption that the c -axis is in-plane (see Fig. 8.1), the dark areas in Fig. 8.4(b) correspond to ferroelectric domain walls in the LMO.

The obvious question here is why we see EFM contrast from the LMO phase at 77 K and not at room temperature. In Fig. 8.5(a) we plot the relative (to 4 K) dielectric loss tangent vs. temperature for a very similar ferroelec-

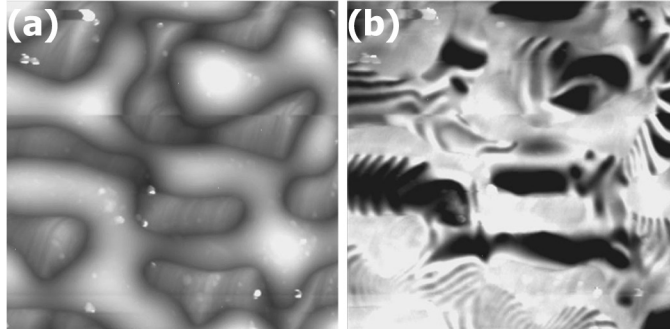


Figure 8.4: (a) Topography (700 nm greyscale) and (b) EFM scan (3 Hz greyscale) of $(\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3)_{0.2}(\text{LuMnO}_3)_{0.8}$ sample at 77 K. Image size: $17 \times 17 \mu\text{m}^2$.

tric material, HoMnO_3 . This is a measure of the lossiness of a dielectric for a given electric field modulation frequency. The losses are generally caused by thermally activated free charge carriers. Based on the increasing losses with temperature in Fig. 8.5(a), we can postulate the the charges at the ferroelectric domain walls are being screened by these free charge carriers at high temperatures. A plot of the EFM contrast that we see in the LMO phase vs. temperature in Fig. 8.5(b) seems to support this assumption; the EFM contrast dies out as the temperature (and the amount of thermally activated screening charges) is increased.

8.3 Future Direction

The future ideas that should be explored with this project are:

1. Is there an interplay between the domain structures in the ferromagnetic

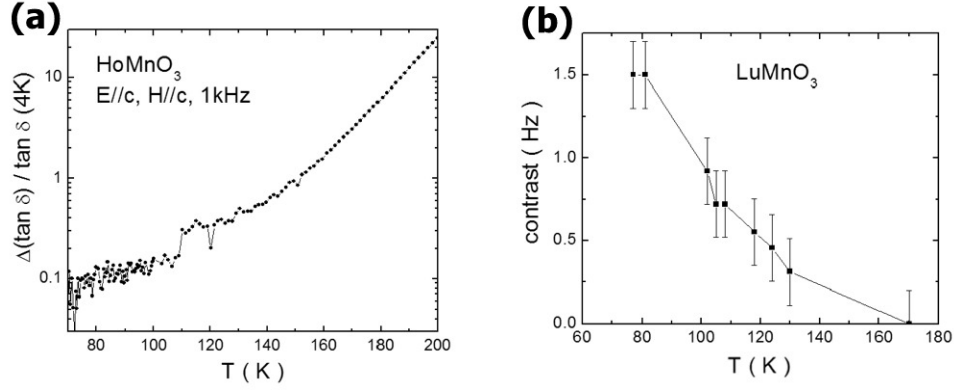


Figure 8.5: (a) Relative (to 4 K) dielectric loss tangent vs. temperature for HoMnO_3 (personal communication, S.-W. Cheong) and (b) EFM contrast in LMO phase vs. temperature.

LSMO and the ferroelectric LMO?

2. Very similarly, if a large electric (magnetic) field is applied, will there be a change in the domain structure in the LSMO (LMO)?
3. Is there a change in the ferroelectric domain structure of the LMO phase or the coupling to the LSMO phase when the LMO becomes antiferromagnetically ordered below $T_N \simeq 90$ K?

Cross-coupling terms in multiferroic systems [63] say that all of these are possibilities, although cursory scans at low temperature do not give any strong supporting evidence.

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