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Imaging Competing Electronic Phases during Metal Insulator Transitions in Transition Metal Oxides using Microwave Impedance Microscopy

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by

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Dissertation

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

The University of Texas at Austin August 2022 **Dedicated to my beloved Parents**

Acknowledgements

I would like to thank Prof Keji Lai. I have been blessed to have an advisor who is not only extremely talented but also humble. I admire his humility, understanding and empathy towards everyone. He treats his students like his own children.

I would like to all my friends and family for their constant support. Specifically, Dr Ajesh Kumar, for being the best friend I could ever wish for, not only was I fortunate enough to be paired with a fellow Physicist as a roommate but also a humble and kind person who was there for me when I needed him. As a theorist, he contributed immensely to my scientific understanding of Condensed Matter Physics. I would like to thank Dr Zhaodong Chu who was a constant source of encouragement and guidance in our lab. The constant motivation he provided us was invaluable and he encouraged everyone to pursue a career in academia. May he achieve his academic goals as we all believe to be fulfilled soon. I was fortunate to work alongside Zhanzhi Jiang who's technical expertise has bolstered the capabilities of our lab and provided a platform to perform my own experiments.

The foundation set up by our group alumni Dr Xiaoyu Wu has paved the path for newer graduate students like me to perform my own independent research on their experimental platforms. Truly, I have stood on the shoulders of giants. Dr Lu Zheng was the first person in our lab to guide and mentor me and I owe him for the smooth beginning of my research career. His intelligence yet humble personality made it easy to interact with him and since he graduated, I missed our cheerful day to day interactions which lead to a positive work environment in our lab. I would also like to thank my fellow lab mates, Mr Xuejian Ma, who I believe has a very bright future ahead of him. Mr Jia Yu, Mr Daehun Lee, Mr Alexander Stram are equally talented and capable to achieve their dreams.

Finally, I would like to thank my family. My parents have been supportive of my academic dreams since I was a kid. My father has always been my hero. He provided our family with everything we needed. Him being a Ph.D. himself has been a source of motivation for me to pursue a doctorate. My brother has always tried to guide me in life in his own way.

Last but not the least, I would like to thank my mother. She has been there for me in every way possible. She is the most wonderful woman I have known and all my accomplishments, past, present and future are all because of her unconditional love and support.

Abstract

Imaging Competing Electronic Phases during Metal Insulator Transitions in Transition Metal Oxides using Microwave Impedance Microscopy

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Abstract: Metal-Insulator transitions are accompanied by huge resistivity changes, sometimes over ten orders of magnitude, and are widely observed in condensed-matter systems. Particularly important are the transitions driven by correlation effects associated with the electron-electron interaction. The insulating phase caused by the correlation effects is known as the Mott Insulator. Despite a long history of investigations, the driving force of the MIT and the exact nature of the ground state are still controversial. Using microwave impedance microscopy, we will study the coexisting metallic and insulating phases in different strongly correlated compounds which might carry important information on the transition in these materials.

In this dissertation, I will begin by discussing Microwave Impedance Microscopy which will be the prime research tool used in the study of these materials. I will present the technical specifications of this tool and how it can be modified to be used on cryogenic setups, mainly, using tuning fork microscopy for topography feedback. The application of MIM to study Metal-Insulator Phase transitions in strongly correlated systems is demonstrated by studying doped Ruthenate oxides. Chapter 4 describes the insights gathered on Ti doped Bilayer Calcium Ruthenates which includes the discovery of a new stripe-phase at the MIT phase boundary. Followed by a chapter discussing the comparison with the MIT in Mn-doped bilayer Calcium ruthenate. I will conclude the dissertation with a short summary of our contribution to the field and an outlook where I would highlight the directions needed to pursue further research and come up with an overall picture of the phase transition in this class of material.

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CHAPTER 1 INTRODUCTION

Science is defined as the intellectual and practical activity encompassing the systematic study of the structure and behavior of the physical and natural world through observation and experiment. We perform experiments and observe and record our findings to derive the underlying mechanism for the cause of the phenomenon. Human beings, since the dawn of time, have used their sense of vision to observe its surroundings. Our vision however is quite limited to observe the various processes of the cosmos. Hence, it requires to be supplemented with specific tools, such as telescopes to observe heavenly bodies, or microscopes to study phenomena which look infinitesimally small to the naked eye.

In the field of Condensed Matter Physics, we study physical properties of matter which arise from forces due to interaction at a nanoscale level. The length and time scale of these phenomena can make it invisible to the naked eye. Hence, centuries of development have led to the inventions of different types of microscopes to aid research in physics.

Using visible light and an arrangement of lenses, optical microscopes magnified objects making them visible to the naked eye and be readily observed. The resolution of optical microscopes depends heavily on the wavelength of the visible light used. The Abbe diffraction limit gives the spatial resolution

$$\Delta \mathbf{X} = \frac{\lambda}{2NA}$$

Where λ is the wavelength of the Electromagnetic wave and NA is the Numerical Aperture of the lenses used.

If we consider the wavelength range of visible light which ranges from 380 to 700 nm, it often fails to sufficiently resolve phenomena at a much smaller length scale which is crucial to perform research in Condensed Matter Physics. Interaction between atoms occurs at a sub-nanometer level. Correlation effects gives rise to patterns and shapes which still range several to tens of nanometers. Hence, new forms of microscopy tools were invented to aid research in this area.

Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM), uses Electrons instead of Photons as their wavelengths are much smaller. Which leads to much better resolution due to the smaller diffraction limit. Atomic force microscope (AFM) generates images by scanning the surface of a sample using an extremely sharp probe whose height is delicately controlled by monitoring the tip-sample interaction. Scientists who invented the above techniques were awarded the Nobel Prize in Physics (1986) in recognition of their contribution pushing the boundary of spatial resolution.

The abbe resolution limit is applicable only to far field microscopes. An alternative pathway for a higher resolution can be achieved by the principles of near field microscopy. In a near field microscope, the source or detector or both are placed at a distance much smaller than the operating wavelength. The resolution limit established by the abbe barrier is broken and only limited by the size of the source or the detector. By pairing the mechanism of near field microscopy to a conventional AFM, several recently invented techniques have contributed to the characterization of strongly correlated phenomena.

Microwave Impedance Microscopy has emerged as a powerful near field microscopy technique which utilizes microwaves to spatially resolve local electrical conductivity and permittivity with sub-micron resolution. Such a technique can contribute to investigate mesoscopic physics involving inhomogeneity in electronic properties such as Quantum Hall effect with conducting and dissipation less edge states, 2D electron gases at interfaces or phase separation during Metal to Mott Insulator transition.

CONDENSED MATTER PHYSICS IN RESEARCH AND INDUSTRY

When dealing with electronic properties of matter, some classifications have arisen. Metals are materials that are good conductors of electricity and heat, while Insulators impede the movement of charge carriers. Much of the modern electronic devices have their working principle based on their tunability from one electronic phase to another. Transistors can be used as a switch and can be turned ON (Low source drain resistance) to OFF (High source drain resistance) which make them one of the most crucial components in any modern electronic device. Memory in the form of bits in a computer can be encoded in a material based on its relative conductivity in each state. Controlling the Metal to Insulator phase transition is a key concept for the design of any electronic device.

By the work done by scientists as Bloch, Sommerfeld and Bethe in 1928 [1], a framework to distinguish metals from insulators was put in place in terms of the Band theory. However, a few Insulators whose properties could not be explained by Band theory were discovered and classified as Mott Insulators. These Mott Insulating states arise due to strong electron-electron correlations and find themselves present in the phase diagram adjacent to other phenomena associated with strong correlations such as superconductivity. Decades of research in all correlated phenomena have propelled investigations in unravelling the nature of Phase transitions from one system to another.

With the use of Scanning probe microscopy techniques, these phase transitions can be directly visualized to gather key insights.

DISSERTATION OUTLINE

Chapter 2 would discuss the technical approach used to perform the research in this dissertation. We would dive in the technical details of Microwave Impedance Microscopy. Beginning with the basic principle of MIM, a step-by-step approach to discuss all the key aspects of a MIM system such as the MIM Electronics. Different types of scanning probes with their pros and cons would be discussed and a special emphasis on Tuning Fork microscopy would be provided. The sections on tip-sample interaction and appropriate simulation techniques would complete this chapter and provide all the information needed to build and operate a homemade MIM tool.

In Chapter 3 a brief review about strongly correlated systems specifically the phenomenon of the Mott Insulating state and its theoretical framework would be provided. A brief history of the research area with an emphasis on the Metal to Mott Insulator transitions with the groundbreaking discoveries in the past two decades, would be crucial in setting up the new avenues to explore in this topic. The significance of scanning probe studies, especially a few based on MIM would be discussed and with it, the potential to explore a few classes of materials would be discussed.

Chapter 4 highlights my contribution to the field of Metal-Insulator transitions for Ruthenates, specifically doped bilayer calcium ruthenates. The results are based on my publication [132]. We discovered an emergence of a competing electronic phase different from the two terminal phases in that system which modifies our understanding of the established phase diagram from previous studies. Chapter 5 includes the follow up work based on changing the nature of the dopant in the parent compound and its effects on the phase separation and the existence of the newly found competing stripe phase. We would compare the nature of the phase transition in both Ti and Mn doped bilayer calcium ruthenates and discuss the underlying causes.

Chapter 6 would conclude this dissertation in summarizing and providing and outlook of the research in this area. Specifically, the steps needed to take to form a theory to explain the behavior we observed for the phase separation, particularly the newly discovered electronic phase.

CHAPTER 2 MICROWAVE IMPEDANCE MICROSCOPY

One of the most common forms of Electromagnetic waves used in day-to-day devices would be Microwave radiation. The term "Micro" comes in comparison to the wavelengths of the most ubiquitous form of EM radiation used prior to Microwave technology which would be Radio waves. They are characterized by wavelengths ranging from 1 millimeter to 1 meter and corresponding frequency between 300 Mhz to 300 Ghz. Our communication networks for our mobile devices such as the wireless network bands (3g,4g,5g) we use to connect to the Internet, all fall into the Microwave region of the EM spectrum. Microwaves are not only used in the operation of these electronic devices but also in the manufacturing. A common method to etch patterns on semiconductors to form an electronic circuit is Plasma Dry Etch process. A plasma is created by energizing a reactive gas using microwave radiation until it ionizes. And that plasma is further used to selectively react with the surface to etch out material and generate patterns. Microwaves have also been used in RADAR as a radiolocation technique where EM waves transmitted from an antenna bounce of objects and return to the transmitter. Due to the wavelength range of Microwaves, they can be used to detect objects ranging in sizes from automobiles to aircrafts.

In any modern society, we bath in a sea of Microwave radiation without even being aware of it and our dependence on it is staggering. For example, a household appliance found in almost every kitchen in the western world would be a Microwave oven, Even the most basic tasks of heating food could be performed using Microwave radiation. Water molecules absorb energy from EM radiation falling in the Microwave range leading to heating of organic materials. However, putting a conductive object in a Microwave oven would be deemed hazardous. It would act as an antenna generating an electric current. If the object has any sharp surfaces, it will result in electric sparks. As a consequence of this property, the microwave radiation is acting as a detector to check if an object is metallic or not.

In this chapter 2 will discuss in detail about Microwave Impedance Microscopy (MIM), a scanning probe tool which combine traditional Atomic Force Microscopy (AFM) with microwave electronics to form a real space mapping of conductivity and permittivity at a nanoscale level [2-5]. Compared to other methods such as Conductive-AFM (C-AFM), which involves a current flow from the sample to the tip, our technique is non-invasive. I will discuss the detailed setup of MIM, its operating principle and the modifications made to investigate strongly correlated systems in a cryogenic environment.

BASIC PRINCIPLE

In a basic MIM setup, the system consists of the following key components. A microwave source to generate frequencies in the range from 100 MHz to 10 GHz. An MIM electronics box which takes input from the microwave source and sends it to an AFM probe and outputs two channels: MIM-Re and MIM-Img. An impedance match to ensure maximum power gets delivered to the tip.

In a nutshell, MIM measures the admittance between a sharp conducting tip and the local region of a sample using microwaves. The tip sample admittance is proportional to the area interacting with the microwaves. The tip confines the microwaves and acts as a source and a detector for a near field microscope. Hence the resolution of MIM is smaller than the diffraction limit typically limited only by the tip aperture size (10-100nm). The microwaves are generated at a source and is delivered to the sample through the MIM electronics. An impedance match network enables maximum microwave power to be transmitted to the tip. The efficiency of the impedance match can be checked using a Vector Network Analyzer (VNA) using a simple S11 measurement.



Figure 2.1: Sketch of an MIM setup.

The output of the MIM electronics are the Real and Imaginary parts of the tip sample impedance which are proportional to the local permittivity and the conductivity. These signals are orthogonal to each other and need to be properly calibrated, usually using conducting Aluminum dot structures placed on an insulating Sapphire substrate generating enough MIM contrast.

MIM ELECTRONICS

Figure 2.2 shows a circuit diagram for the microwave electronics. The Microwave power coming from the microwave source is split into three lines using two splitters. The first line goes to the scanning probe tip through an impedance match network. The reflected signals are picked up by the same tip acting as both a transmitter and receiver. A coupler makes sure that the reflected signals do not go back to the microwave source. A Bias-T can be added to add a bias voltage to the tip while scanning. This can be useful for

parallel C-AFM scanning or to switch the polarity of a ferroelectric with an applied tip voltage. However, for a typical MIM scan, this component is not necessary.



Figure 2.2: Detailed MIM Electronics

The reflected signal contains a huge background signal. This common mode signal comes from the internal and external reflections from the electronics and the sample. Typically, we are only interested in the relative conductive and permittivity of a scanned area to its adjacent region. Hence, the parameter to track would be the change in the reflected signal. Hence, using another coupler we add a cancellation signal so as to get rid of the constant background and are left with only the small change. An attenuator and a phase shifter are used to adjust the cancellation signal match in amplitude and to be opposite in phase with the common mode signal to cancel it.

Since the signal strength is quite small, it passes through a series of AC amplifiers, usually three and then demodulated using an IQ mixer. The third split from the microwave source goes to this IQ mixer which splits the reflected signal into two

orthogonal components. With an appropriate calibration using another phase shifter, the two components can be tuned to MIM-Real and MIM-Imaginary parts. Another set of DC amplifiers is used to boost the signal before generating an output.

Typically, this entire set of Microwave electronics is built inside a box with an external custom-made power supply for some of the components such as the AC and DC amplifiers. To fine tune the cancellation signal, we need to monitor the signal as we adjust the amplitude and the phase using the attenuator and a phase shifter. For that purpose, we could add a coupler before the AC amplification stage, one of the outputs of the coupler can be used to create a monitoring port which can be connected to a spectrum analyzer. Another monitoring port can be created similarly after the ac amplification stage to fine tune the cancellation. An MIM electronics box can be created to operate in a range of different frequencies based on the specifications of the components used. Typically, a separate electronics box is made to operate around 100Mhz, 300Mhz 1Ghz, 3Ghz and 10Ghz frequencies.

For the room temperature setup, this MIM electronics box operates in conjunction with a commercial AFM platform (Park XE-70). There are two sources of noise: Johnson–Nyquist noise which is the electronic noise generated by the thermal agitation of the charge carriers (usually the electrons) inside an electrical conductor at equilibrium, which happens regardless of any applied voltage. The other one being Shot noise which originates from the discrete nature of electric charge.

If we consider a bandwidth of 1Khz and the impedance to be 50Ω . The Johnson noise can be calculated from the following formula.

$$V_{J} = \sqrt{4k * T * B * R}$$
$$= \sqrt{4k * 300K * 1Khz * 50\Omega}$$
$$= 30 \text{ mV}$$

and shot noise considering a 20mV input voltage

$$V_{\rm S} = \sqrt{2 * e * V * B * R}$$
$$= \sqrt{2 * 0.02V * 1 \text{kHz} * 50\Omega}$$
$$= 20 \text{mV}$$

Typically, the gain of the RF and DC amplifiers is about 106db (2*10⁵). So our total noise level would be

$$V_{\rm N} = G * (V_{\rm J} + V_{\rm S})$$
$$= 10 {\rm mV}$$

This would be the sensitivity that can be achieved at Room temperature. In cryogenic environments, the Johnson noise can be lowered further because of its dependency on temperature. Hence the sensitivity level can be improved by placing the electronic components in the cryogenic chamber alongside the sample. Since the space in a typical low temperature system is limited, not all components could fit in the chamber volume. Hence, the section of the MIM electronics box including the two couplers used alongside an RF amplifier is placed in a chamber of a system that can operate at low temperatures.

SCANNING PROBES

One of the most critical components of a Microwave Impedance Microscopy setup is the AFM platform which works concurrently with the MIM electronics. For this purpose, an AFM probe which is compatible to deliver and receive microwave signals from the sample is necessary. These probes must have a conductive line from the cantilever to the tip so that it can be used as a near field antenna while scanning. There is a wide range compatible Conductive AFM (C-AFM) probes which are commercially available and compatible with standard AFM systems. Some of these probes are compatible with MIM but they generate stray fields from the cantilever body. A perfect probe would have only the tip apex interacting with the sample. A microfabricated probe with a shielded conducting stripline would be ideal for MIM. To ensure maximum sensitivity to minute changes in the tip sample interaction, low series resistivity and background capacitance is desirable. Commercially produced probes, which offer all these features, will ensure consistent probe performance, and will also make the process economically viable.



Figure 2.3: Different types of MIM probes (a) Top: Schematic of a gold metal pad attached to a conducting cantilever. Bottom: Picture of the cantilever with a tall shank. Inset shows SEM image of the tip. (b) Top: Schematic of the shielded cantilever with a conducting stripline leading to the tip. Bottom: SEM image of the cantilever. Inset shows sharpness of the tip. (c) Top: Picture shows oscillation of a tuning fork. Bottom: An etched tungsten wire glues to one of the prongs of the tuning fork. Inset SEM image shows sharpness of the etched wire.

Figure 2.3 shows different types of probes that can be used for MIM measurement. Figure 2.3(a) is a probe made available commercially by Rocky Mountain Nanotechnology LLC. As discussed earlier, transmission of microwave signals through

an unshielded cantilever could generate stray field noise from the cantilever and the sample interaction. However, if the distance between them is large enough to mitigate the effects of the stray field coupling, the probe could be suitable for an MIM scan [6,7]. In these probes, the cantilever is about 80um away from the tip. These probes are quite flexible and can also be used in contact mode without feedback, which could be the case for a home built cryogenic system. The approach of the tip to the sample is guided by the sudden jump in MIM signal when tip-sample contact is initiated.

Figure 2.3(b) is the most widely used commercially available MIM probe provided by Prime Nano Inc. Another way to mitigate the effects of the stray field is to create a strip-line for the microwaves. With a series resistance of $< 5\Omega$ and capacitance of about 1pf made of Au/Ti/W conductor encapsulated with a SiN_x dielectric shielding, these strip-lines have been optimized to ensure maximum sensitivity to tip sample interaction. The tip diameter is < 100nm which is created by oxidation sharpening of the sacrificial Si pit and the subsequent metal refill. The structure of the cantilever is designed to be symmetric to balance the stress and thermal expansion on both sides, keeping cantilever straight in variable-temperature experiments. Advanced MEMS technology makes consistent large-scale manufacturing of these tips economically efficient. Additional information can be found in ref [8]. These Gen 5 tips are also suitable for Conductive Atomic Force Microscopy (C-AFM) and Piezoresponse Force Microscopy (PFM) experiments due to their ability to apply external potential bias to the tip.

Frequent contact mode scanning could inevitably increase the radius of the tip apex which strongly affects both the electronic and spatial sensitivity. Another drawback would be the need of a laser feedback system to maintain tip sample distance which involves bulky electronics that may not accommodate in the confines of a cryostat for low temperature experiments. Optical alignment is also necessary which is susceptible to thermal drift. A quartz tuning fork offers an innovative way to perform non-contact based AFM. By attaching an electrochemically etched metal wire, its self-sensing capability is based on the change in drive-amplitude or frequency response from the tip-sample interaction. Figure 2.3 (c) shows the high aspect ratio which accounts for the lack of shielding of the conductive channel for the microwave signal.[9]

Each of these probes have their benefits regarding the specifications of the experimental project. Commercial probes are rather expensive, yet they offer consistent and reliable performance at room temperature due to their compatibility with ubiquitous AFM systems. The Gen 5 Prime Nano Inc tip is suitable for most room temperature operations except for Laser-Assisted MIM. The multi layered shielding has a strong expansive effect from the excitation beam leading to cantilever degradation over time. The Rocky Mountain probes have cantilevers made from a single metallic layer and hence are more suitable for this application. The self-sensing capability of TF probe allows for distance modulation which rejects the background signal drift which is prone to stray coupling. It is also possible to extract the absolute information about the dielectric constants at every point.

TUNING FORK-BASED SPM

In this dissertation all MIM data is gathered using Tuning fork-based Scanning Probe Microscopy in conjunction with Microwave electronics for MIM imaging. In this section I will discuss the technical details of this specific mode of operation and its benefits. An electrochemically etched metal tip, usually Tungsten or Platinum/Iridium is used to glue to one of the prongs of the tuning fork. While the other end of the wire is connected using solder to a coaxial cable connected to the impedance match and microwave electronics. In case of Tungsten, the wire is usually plated with a thin layer of gold because of its affinity to form a solder bond.



PLL PID Φ attn Attn, θ Mìxei ∕1/\∕ Amplifier Coupler 🕶 Z match -Oscillator Sample Piezo В Z servo stack

Figure 2.4: TF-based MIM probe: (a) Image of the Tuning fork based. Inset shows the prong on which the wire is attached with super glue. (b) SEM image of the etched tip with length of the conical region around 100 um. Adapted from Ref. 9. (c) Schematic of tuning fork-based AFM for self-sensing and microwave electronics.

The quartz tuning fork has been widely used by the AFM community in cryogenic environments due to its self-sensing capability [10,11]. Due to which parameters such as dithering amplitude of 10-15nm, wire thickness of 25 um has been optimized to conserve spatial resolution and provide ample topographical feedback to account for surface roughness. TF-MIM has been recently developed and has been widely used for cryogenic experiments [12,13].

Frequency modulation is a popular mode of operation non-contact based SPM especially for STM operations in high vacuum and cryogenic environment [14]. However, they operate with small vibrational amplitude to stay in the attractive or the repulsive distance regime of the tip sample force. This requires the sample to be with low surface roughness (< 2nm), however samples for many MIM studies have a surface roughness of about 10-100nm. In which case, the tip-sample force might jump from attractive to repulsive regimes. The non-monotonic behavior of the atomic fore interaction could lead to instability of the feedback control. Driving amplitude modulation mode (DAM-AFM) has been developed as an alternative way for topographical feedback based on power dissipation [15]. The power dissipation is monotonic and only depends on the vibration amplitude making it the ideal choice for rough surface and high noise environment.

Figure 2.4(c) shows the schematic of the drive amplitude modulation mode for self-sensing feedback control combined with MIM electronics. In this implementation, a driving resonant frequency (~ 40KHz) is sent to the tuning fork to generate a vibrational amplitude of around 10-15nm. It should be noted that gluing an etched metal wire reduces the q-factor of the Tuning fork due to the apparent asymmetry in the weights of the prongs. The TF signal is detected by a current to voltage amplifier (I/V) connected to a Nanonis SPM control system. The output measures the phase shift and the amplitude of

vibration which is kept constant using a Phase Lock Loop (PLL) and a Proportional Integral Derivative (PID) respectively. In the drive amplitude modulation mode (DAM) the setpoint of the excitation voltage in kept about 10-15% above the free oscillation voltage required to maintain the desired amplitude. This ensures constant power dissipation in a tapping mode AFM scan. The output of the PLL and PID loops is fed to the z-controller of the piezo stack to maintain a constant average tip-sample distance. The DAM mode offers significantly better performance for feedback stability compared to the FM mode [16]. The other end of the etched wire is solder to a coaxial cable connected to the MIM electronics. The MIM signals would be modulated at the TF operating frequency and hence a reference signal is used at the output channels for demodulation to generate the MIM Img/Re AC signals.





Figure 2.5: Tip etching details (a) Tip etching setup. (b) SEM image of W wire (c) SEM image of Ni wire. Scale bar - 100um

The recipe for electrochemically etching W or Pt/Ir wires has been widely established in the STM community [17]. Electrochemical etching creates a sharp tip apex

required to generate atomic level resolution for STM scans and hence are capable of sufficiently resolve mesoscopic features for MIM.

Figure 2.5(a) shows a typical Tip etching setup. The process of electrochemical etching involves applying a potential bias between the tip acting as an anode and a circular electrode acting as an cathode. A thin film of electrolytic solution (NaOH) is pierced by the metal wire and the electrochemical reaction occurs at the intersection of the wire and the solution.

The following indicates the reaction at the cathode and anode for a Tungsten (W) wire etch.

Cathode: $6H_2O + 6e^- \rightarrow 6OH^- + 3H_2$

Anode: W + 8OH⁻ \rightarrow WO₄²⁻ + 4H₂O +6e⁻

By the application of a dc voltage (V_{dc}), a current flow initiates etching of the tungsten wire. The reaction can be observed when H₂ bubbles are generated at the cathode. The length of the wire hanging below that point acts as a weight that stretches the wire into a conical shape as it weakens while it is undergoing the reaction and eventually falls off. To ensure a sharp tip apex, the cutoff current I_{cutoff} is adjusted so the reaction stops exactly at this event. Properly adjusting the parameters of this procedure could consistently generate tip apex of around 100nm or less [18]. During the process, Tungsten oxide is generated around the anode which forms a protective layer around the tip. This limits the etching only around the intersection point of the solution and the wire. Over time, this oxide layer would develop if the tip were stored in an oxygen-rich environment. The oxide layer could lower the tip quality and increase the apex size; hence glovebox storage is recommended. Additionally, gold plated tungsten wires could be used which provides protection from oxidation and allows easy soldering compared to Tungsten wires. Similar procedures for Ni tip etching have also been established for Spin

polarized STM applications [19]. These Nickel tips can also be repurposed for Magnetic Force Microscopy (MFM) [20].

IMPEDANCE MATCH

If the MIM electronics is directly connected to the tip, a considerable amount of microwave power could get reflected from the tip itself instead of interacting with the sample. The reflection coefficient Γ is a measure of the power reflected from the load impedance Z_L connected to a transmission line with impedance Z_0 will be

 $\Gamma = (Z_L - Z_O) \div (Z_L + Z_O)$

For a uniform transmission line, the characteristic impedance Z_0 is 50 Ω . For a perfect transmission of microwave power, the load needs to have the same characteristic impedance. However, not every microwave component would have the same impedance. For example, the Gen 5 tip that is the most widely used tip for MIM has -150i Ω of impedance at around 1GHz. This mismatch between the tip and the transmission line can be dealt by adding an "Impedance matching" component between them. This Impedance matching component adds a circuit of series or parallel resistors, capacitors, or inductors to tune the load impedance to match the transmission line.



Figure 2.6: Impedance matching network for 1Ghz microwave frequency.

Figure 2.6 shows a typical impedance match circuit used at 1Ghz frequency and higher harmonics of 3Ghz, 5Ghz $(3\omega, 5\omega)$ etc. A quarter wave coaxial cable is connected in series whose length is determined by the wavelength of the desired microwave operating frequency. This quarter wave cable is flexible (Astro-Boa-Flex III, Astrolab Inc.) and is connected to the MIM tip by wire bonding the center cable to the strip-line bonding pad. An open-ended coaxial cable stub (Micro-Coax, UT-085C-TP) is connected in parallel so as to adjust the impedance of the network to 50Ω . The benefit of this arrangement is the tunability of the impedance from this stub. This Impedance match section in conjunction with the tip can be connected to a Vector Network Analyzer (VNA) to monitor the S_{11} signal as we trim the length of the tuning stub. For each value of the open stub length, the VNA displays S11 as a function of frequency. The length is adjusted until an observed dip in the VNA signal that measures the reflected power is at its maximum. The frequency corresponding to this dip is chosen to be the MIM operating frequency. By ensuring maximum power transfer to the tip, the sensitivity to the tipsample admittance is optimized. More information about different impedance matching networks for different frequencies can be found in ref [21]



Figure 2.7: Impedance matching network for 1Ghz microwave frequency using a capacitive element.

One of the drawbacks of the impedance match setup using variable length tuning stub is highlighted during cryogenic experiments. Due to the change in dimensions of the stub due to contraction at low temperature, the Impedance match operating frequency based on the S_{11} dip has been observed to shift. Change in the reflection coefficient Γ has also been observed to increase affecting the sensitivity level. Hence an alternative Impedance match configuration has been proposed. Figure 2.7 shows a capacitive element of 0.2-0.3pf which is connected in series to a half wave coaxial cable. With the appropriate capacitors with reliable cryogenic performance, the stability of this capacitor-based impedance matching network is much superior compared to the tuning stub configuration.

For the tuning fork probe, the effective impedance can be calculated by a lumped element analysis. At 1 GHz, the tip would have an effective impedance based on resistance of $R_{tip} = 1\Omega$, capacitance $C_{tip} = 0.16pF$, and inductance $L_{tip} = 10nH$ connected in series. The impedance (Z) match circuit would hence consist of a flexible quarter-wave cable (Astro-Boa-Flex III, Astrolab Inc.) of 4.8 cm and a semi-rigid tuning stub (Micro-Coax, UT-085C-TP) of 6.0 cm which can be replaced by a 0.2-0.3 pF capacitor which would tune the operating frequency between 0.9-1.1Ghz. Impedance matching is a crucial
topic in microwave engineering and interested readers can go through the famous textbook by Prof David Pozar for additional details [21].

TIP-SAMPLE INTERACTION

To understand how the change in local electronical properties is detected by the MIM circuitry, a thorough understanding of the Tip-Sample interaction is necessary. The electrical properties of the sample affect the impedance between the probe and the sample $(Z_{Tip-Sample})$. A commonly used technique to image local conductivity is Conductive-AFM (C-AFM). This technique directly measures the local electrical properties by drawing an electrical current from the sample to the tip used as an electrode and measuring the local resistivity. However, this straightforward implementation has some drawbacks, particularly its invasiveness and limitations because the resolution is determined by the local conductivity. The contact resistance also needs to be low for the tip-sample interaction to be dominated by the sample resistance. An oxide layer readily forms on metallic compounds and on Insulating or semiconducting samples, a Schottky barrier is formed due to the depletion region. Achieving a low enough contact resistance hence becomes challenging.

The MIM technique is built upon the fundamentals of the Capacitance measurements. Hence the Tip-Sample impedance is based on the capacitance between the tip apex and the local region of the sample ($C_{Tip-Sample}$). The capacitance would depend on the ability of the local sample surface to screen and reflect the incoming microwaves from the tip apex which in turn depends on the complex permittivity,

$$\varepsilon = \varepsilon^{r} + i(\varepsilon^{I} + \sigma/\omega)$$

Where ε^{r} is the real part of the dielectric constant and the ε^{I} is the imaginary part which characterizes the dielectric loss, σ is the conductivity and ω is the frequency. An oxide

layer on samples acts as a capacitor hence blocks only DC measurement and does not impede AC frequency used by MIM.



Figure 2.8: Equivalent circuit to model the Tip-Sample Interaction.

Figure 2.8 shows an equivalent circuit model to describe the tip-sample interaction. Since the tip-sample distance is at a much smaller distance compared to the wavelength of the microwaves used, we can use the quasi-static limit and used lumped sum elements. The interaction is determined by the impedance which can be described as a combination of capacitance and resistance elements. The tip sample impedance is Z_{Tip} -sample and its inverse is the admittance Y_{Tip} -sample or Y_{T-S} . This admittance evolves as a function of the location during the scan as the contribution is from the tip and a few hundred nanometers around the tip apex. The impedance and its inverse admittance of the tip Y_{T} can be considered as constant. The total admittance of the terminal would be $Y_{Total} = Y_{T-S} + Y_{T}$.

An incident microwave radiation is sent from the probe to interact with the sample and the reflected signal is analyzed. The amount of reflection depends on the reflection coefficient Γ . The coefficient can be calculated using Impedance of the

transmission line and the load as shown earlier, but a similar relation using admittances can also be used.

$$\Gamma = (Y_0 - Y_{total}) / (Y_0 + Y_{total})$$

Where Y_0 is the transmission admittance of $(50\Omega)^{-1}$. The reflection could be very high due to mismatch in the admittances. Using the Impedance match network described in the previous section, the total admittance is transformed from Y_{total} into $f(Y_{total})$ with the value close to Y_0 . Hence, the reflection coefficient becomes.

$$\Gamma = (Y_0 - f(Y_{total})) / (Y_0 + f(Y_{total}))$$

The reflected MIM signal would have two components MIM-Re which denotes the real part and MIM-Im denoting the Imaginary component. To separate these components, the MIM signal needs to be demodulated at a reference phase ϕ with respect to the incident signal:

$$\begin{split} \mathbf{MIM} &= V_{in} \, e^{i\phi} \, \Gamma \\ &= V_{in} \, e^{i\phi} \left(Y_0 - \mathbf{f}(Y_{total}) \right) / \left(Y_0 + \mathbf{f}(Y_{total}) \right) \\ &= e^{i\phi} \mathbf{F}(Y_{total}) \end{split}$$

When calculating the total admittance, the contribution from the tip-sample interaction is much smaller compared to the tip itself. This is due to size of the tip-sample interaction region compared to the tip. We can use Taylor series expansion of the total admittance and treat the tip-sample interaction admittance as a small perturbation to it: MIM $\approx e^{i\phi} F(Y_{total}) + e^{i\phi} F'(Y_{total}) Y_{T-S}$ = kY_{T-S} +b Here k = $e^{i\phi} F'(Y_{total})$ and b = $e^{i\phi} F(Y_{total})$.

When we analyze the MIM signals reflected by the sample, we are interested in the variation of the signal rather than its absolute value to generate a contrast in our images, so a more useful form is:

$$\Delta MIM = k \Delta Y_{T-S}$$

We can write the same relationship in a more explicit way, describing the real and imaginary parts of the MIM signal:

$$\Delta$$
(MIM-Re) = k Re(Δ Y_{T-S}) and Δ (MIM-Im) = k Im(Δ Y_{T-S})

Where k can be made into a real number by adjusting the phase. A rigorous proof can be found in ref [22].

MODELLING OF TIP-SAMPLE INTERACTION

As we proved in the earlier section, the MIM channel strengths is proportional to the real and imaginary parts of the tip-sample admittance. Y_{T-S} in turn depends on the local sample region around the tip apex. In principle, the microwaves would be reflected from the sample and the reflection coefficients can be calculated by Maxwell equations with the right boundary conditions. A numerical solution can be calculated by using finite

element analysis which involves dividing the region of interest in different sections. Certain software's are specialized in generating simulations for Electromagnetic waves and one particularly popular commercial FEA tool is COMSOL Multiphysics simulation software. In this section, I will outline the steps to generate simulations and generate tipsample admittance with varying local sample resistivity in COMSOL.

The procedure for all versions of COMSOL are similar and are as follows:

- 1. First, choose the 2D-axisymmetric mode Tis reduces computational time if the sample is rotationally symmetric.
- 2. To build a model, we need to use the Physics tab/Add Physics and then in the pop-up window choose AC/DC > Electric Current mode > Frequency Domains (in previous versions: quasi-static, electric > Electric Currents > time-harmonic analysis). This model will compute the high-frequency quasi-static potential distribution between two electrodes.
- 3. Use the Geometry option to draw half of the tip and sample inside a large box representing the air around the tip. The tip dimensions are around 2 μm tall and 100 nm radius at the apex and draw a box indicating the sample depth 100 μm.



Figure 2.9: MIM simulation model (a) Drawn tip and sample geometry for the model. (b) Generated mesh for finite element analysis. (c) Potential distribution between the tip and the sample.

- 4. Specify the value of the dielectric constant and conductivity of each region and the boundary conditions.
- 5. Specify the boundaries condition.
 - a. Tip: Terminal 1, Voltage = 1 V (red). Terminal 1 represents the incoming Microwave signal.
 - b. The air and sample boxes: Terminal 2 Voltage = 0 V (blue). Terminal 2 represents the ground at the distance far away from the tip.
- Now we need to generate the mesh for finite element analysis. Use Mesh menu in Geometry. A finer mesh setting gives more accurate results but increases computing time.
- 7. Specify the frequency by choosing the operating frequency.

- 8. Compute the solution and obtain the potential distribution. (This step could take a few hours depending on the computing power.)
- 9. Obtain the real and imaginary parts of the tip-ground admittance Y21, which is built in and can be found in Derived Values > Global Evaluation> Admittances.



Figure 2.10: Simulated MIM curves for the Real and Imaginary output as a function of the sample resistivity.

Figure 2.10 shows how the Real and Imaginary output channels of the MIM signal change with the local sample resistivity. These are the simulated real and imaginary parts of the tip sample impedance which as we had shown earlier, are directly related to the MIM-Re and MIM-Img channels. Our sensitivity is maximized around the peak of the Real part channel. It is necessary that the conductivity contrast generated by

the phenomenon we plan to investigate should fall around this sensitivity window so that our MIM images can record the apparent change in both channels. This simulation was performed for an operating frequency of 1 GHz but using a higher frequency shifts the peak towards higher conductivity.

PRINCIPLE OF A PULSE TUBE CRYOCOOLER

In this dissertation, we investigate Strongly Correlated Phenomenon which are only accessible at cryogenic temperatures [23]. These phenomena appear only at a certain temperature window as well as be tuned by external Magnetic Field. For this purpose, we use a modified Cryomech Attodry 1100 pulse tube cryocooler to incorporate MIM in a cryogenic environment. In this section I will describe the functioning of a pulse tube cryocooler and the modified MIM assembly.

The cryogenic refrigeration system operates on the principle of a closed-loop helium expansion cycle. The systems major component would be the compressor package and the refrigerant which removes heat from the system. The cold head is the coldest part of the system which uses the refrigerant to extract heat. The refrigerant gas used needs to be in the gaseous state to the lowest possible temperatures, hence highly pure helium gas is used in Cryomech systems. There are two connection lines to the cold head from the compressor, one is the low-pressure line which absorbs heat and a high-pressure line which flows back to the cold head from the compressor.

Heat exchange is carried out in the following steps. The low-pressure helium is compressed by an oil-lubricated compressor and returns it to the cold head. When the gas is compressed, the heat is removed via a heat exchanger which is connected to the compressor with a flow of distilled water. The oil from the compression process is removed in a series of oil separators and filters. The compressed helium is then fed to the cold head via the high-pressure helium flex line.

In the cold head, adiabatic expansion of the helium and further heat removal allows cooling to cryogenic temperatures.



Figure 2.11: Schematic of a pulse tube cooler. Pulse tube coolers cool by compressing and displacing a working gas on a periodic basis. In case of the attoDRY1100, this is achieved with a compressor, two Helium pressure lines and the pulse tube cooler valve.

A pulse tube cooler consists of a regenerator which contains a porous material. It is connected to the cold end of the pulse tube. At the warm end, the pulse tube is connected to a buffer volume by an orifice. The buffer volume is large enough to neglect the oscillating pressure variations. The gas flow through the orifice separates the heating and the cooling effects. Figure 2.11 shows a schematic of a pulse tube cooler.

During the first step, the piston moves towards the regenerator and compresses the gas. The generated heat is removed by a heat exchanger to the cooling water circuit. The gas flows to the buffer and the regenerator takes heat out of the gas while flowing through the porous magnetic material. At the warm end of the pulse tube the gas flows through the orifice and gives heat to the surroundings.



Figure 2.12: Cryogenic MIM setup (a) Attodry 1100 cryocooler (b) Insert stick with Tuning fork probe and XYZ piezo positioners and scanners. Red ellipse shows the sample holder.

During the expansion process, the piston increases the volume. The gas temperature is reduced as it flows out of the reservoir, through the orifice and removes heat from the regenerator. The function of the pulse tube is to separate the warm end the cold end. Therefore, the tube must be large enough that the gas travels only a part of the tube length. The gas in the middle of the pulse tube forms an insulating barrier between the cold end and the warm end because it never leaves the pulse tube. The gas at the cold end will never reach the warm end. Figure 2.12 (a) shows the Attodry 1100 system. The cryocooler has two vacuum chambers, one enclosing the other. Figure 2.12 (b) shows an insert capable of holding a Tuning fork probe, an XYZ piezo stack consisting of Positioners and Scanners with a sample holder on top of it. The MIM Impedance match along with a few MIM electronics which include some AC amplifiers and direction couplers can also be included in the stick so that the Johnson noise contribution is reduced at low temperatures.

SUMMARY

In this section, we have discussed in detail about the MIM technique. From its foundations based in scanning probe microscopy, we talked about various kinds of MIM probes, commonly used MIM electronics and the general principle behind the tip-sample interaction. For cryogenic experiments, the benefits of a tuning fork-based probe and pulse tube cryocooler whose functioning is not time constrained by the amount of liquid cryogen available.

MIM has been demonstrated to be a very versatile tool [24]. Particularly, the TF-MIM cryogenic operation opens doors to explore low temperature condensed matter phenomenon. The local conductivity imaging has been used to study Phase transitions in Strongly correlated materials [25]. In latter chapters, we will explore this further and contribute to this field by adding key insights in our investigations of Metal-Insulator transitions in Strongly correlated materials.

CHAPTER 3

MOTT PHYSICS, METAL-INSULATOR TRANSITIONS AND SCANNING PROBE MICROSCOPY

Metals and insulators are different states of matter which can be distinguished based on the Fermi level. For Insulators the Fermi level lies within the bandgap and for metal it resides within a band. This has been established based on Conventional Band theory [26]. A more common way to classify Metals and Insulators is based on the change in resistivity with respect to temperature. For Insulator, resistivity increases with decreasing temperature as carriers have less energy to jump to the closest unoccupied band, while for the metals, resistivity decreases with decreasing temperature as the thermal velocity of an electron depends on temperature which leads to fewer collisions between electrons and atoms. Such a simple picture was challenged even in the early days of solid-state physics by the discovery of unexpected insulating or metallic states in transition-metal oxides, e.g., NiO [29, 30]. Efforts to explain such anomalies launched the decades long investigations in strongly correlated electron systems. It is now widely accepted that metal-insulator transitions (MITs) are closely related to other exotic phenomena such as unconventional superconductivity, colossal magnetoresistance, quantum criticality, charge/orbital ordering, etc [28]. In addition to the scientific merit, MITs are also attractive for device applications that take advantage of the drastic resistivity change. Research in this area will continue to flourish and the knowledge will foster the growth of energy science and technology.

BAND THEORY AND ITS ASSUMPTIONS

Before we proceed to discuss Mott Insulators, we need to discuss the preceding theories and its shortcomings. The standard model is based on electrons travelling as Bloch waves and being delocalized throughout the lattice. Reviewing the Bloch-Wilson band theory, which is used to calculate the electronic nature of solid-state materials, we come across a few key assumptions:

- 1) The lattice is assumed to be periodic.
- Electron-Electron interaction is neglected or averaged out by using the Hartree-Fock approximation.
- 3) Lattice vibrations are neglected, or weak electron-phonon coupling can be added as a perturbative calculation.



Figure 3.1: Categorizing materials into Metals, Insulators and Semiconductors depending on the location of the Fermi level and Band structure.

These assumptions lead to a simplistic model. Periodicity of lattice leads to making momentum (k) a good quantum number. Once the band structure and fermi level are calculated, the classification become simple. Figure 3.1 shows different configurations of the overlap between conduction and valence bands and the Fermi level. In a partially filled band, electrons are free to move in an external electric field which

leads to metallic behavior. In insulators, a band gap prevents electrons from jumping to the next available state and localize electrons. This bandgap however is lower in semiconductors, in which slight doping and introduction of in-gap states could drastically affect the conductivity making it ideal materials for electronically tunable devices.

But these assumptions fail to explain certain phenomenon. In case of disorder, in which the lattice loses its periodicity, certain levels of disorder could lead to an Anderson localization state. A band theory picture is therefore difficult to calculate for an amorphous phase of a material. In Band theory, the behavior of an electron is envisioned as a single electron travelling as a Bloch wave which is only dependent on the periodic lattice potential and neglects correlations coming from the onsite valence electrons.

HUBBARD MODEL AND MOTT PHYSICS

In 1949, Sir Neville Mott pointed out the fatal flaws of Band theory when trying to explain experimental phenomenon of certain compounds such as those of the Nickel oxides [31,88]. These materials would be classified as Mott insulators and defined as "Insulators whose properties could not be explained by the standard band model by Bloch-Wilson" and Mott transitions as "Transition from a metal to a Mott Insulator".

The approach to explain this insulating behavior was led by considering the coulomb repulsion between electrons. Inspired by Wigner crystallization, which is a predecessor to a Mott insulator, in which an interacting electron gas forms a periodic crystal-like state to maximize the distance between them to reduce the potential energy of the overall system. The periodic arrangement leads to localization of electrons and hence an insulating nature. This qualitative reasoning by Mott was theoretically explained in the much-celebrated Hubbard model. The transition between metal to Mott insulator phase can be understood by considering a simplistic case of a 2D-fermionic lattice.



Figure 3.2: A 2D-lattice representing the Hubbard model. The overlap between orbitals determining the hopping parameter **t** and on-site correlation **U** contributing to the potential energy of the system.

The Figure 3.2 illustrates a 2d lattice with each site able to accommodate 2 electrons. Here t, U and μ denote the transfer integral, the onsite Coulomb correlation, and the chemical potential respectively. This approach explains the insulating behavior was led by considering the coulomb repulsion between electrons and the overlap between orbitals which leads to the hopping between lattice points.

The Hubbard Hamiltonian is as follows:

$$H = -t \sum (c^{+}{}_{i\sigma}c{}_{j\sigma} + h.c) + U \sum n_{i\uparrow}n_{i\downarrow} - \mu \sum c^{+}{}_{i\sigma}c{}_{i\sigma}$$

 $c^{+}{}_{i\sigma}$ and $c_{j\sigma}$ represent the creation and annihilation operators at site i and j respectively. The first term represents the kinetic energy contribution from the hoping of electrons from one site to another. Usually, only the nearest neighbors hoping is considered. The transfer integral t is proportional to the overlap between the nearest neighbor orbitals. Figure 3.2 shows the orbital overlap region which is susceptible to the lattice spacing. The potential energy contribution is from the second term which represents the coulombic repulsion from the onsite electrons, which is usually neglected in band theory calculations. The third term controls the filling factor of the lattice. We can imagine that at exactly half filling, an energy gap proportional to U would be needed to allow electron hoping to another site and hence gives rise to an insulating nature. One of the most important advantages of this model is that the electronic states and the low-energy charge dynamics at low temperatures can be roughly described despite its quite simple formation.

In most systems exhibiting MITs, neither the insulating nor the metallic phases can be well described by the non-interacting band theory. For transition-metal compounds, the correlation effect may split the partially filled d-band, resulting in the Mott-Hubbard insulator [32, 33] with a charge excitation gap between the occupied lower Hubbard band (LHB) and unoccupied upper Hubbard band (UHB).



Figure 3.3: Illustration of d-band splitting due to Onsite Interaction.

In some materials, the p-band of ligand atoms may be above the LHB, resulting in the charge-transfer insulator [33]. At the same time, metallic states near the transition also display unusual charge dynamics that are far away from the standard Fermi-liquid picture [28]. The electronic states here are mostly localized rather than itinerant due to the strong charge, spin, and orbital fluctuations.

METAL TO MOTT INSULATOR TRANSITION

The Hubbard model described earlier can be used in its most simplistic form for a single band encompassing all the information in the parameters U, t and μ . The ratio U/t can solely determine if the system can be in a Mott insulating phase or not while the parameter μ is used to control the filling factor to tune the system in and out of the Mott state. Figure 3.4 adapted from reference [28], describes the phase diagram based on the parameters of the Hubbard Hamiltonian.



Figure 3.4: Metal-Insulator transition phase diagrams based on the parameters of the Hubbard Hamiltonian and routes for transition across the phase boundary.[28]

As schematically shown in Figure 3.4, the transition can be classified into bandwidth control (BC)-MIT, where the process is driven by the correlation strength (Coulomb repulsion versus the hopping integral). In the bandwidth control mechanism, the overlap between orbitals could be increased which leads to an increase in the hopping parameter (t) which represents the kinetic energy of the system. The width of the bands is directly proportional to the hoping parameter (t) and when the bands widen enough to accommodate the fermi level, the system becomes metallic. For the filling control (FC)-MIT, the process is driven by doping of charge carriers. Doping can change the fermi level itself and can be tuned to lie within a band, hence making the system metallic. Near certain commensurate fillings, the compound may also undergo another type of transition known as the charge-ordering (CO)-MIT. Figure 3.5 illustrates how controlling the Fermi level leads to a transition from a Mott Insulating state to a metallic state for mechanisms mentioned above.



Figure 3.5: Depiction of Mott Insulator to Metal transitions by different mechanisms.

OXIDE MOTT INSULATORS

The doping of charge carriers in the periodic lattice described earlier gives rise to a dual nature of the material in which the system can be tuned in and out of a Mott insulating state. This duality is most apparent in Transition metal oxides in which strong electron-electron correlations will determine the electronic properties of the material. In transition metal oxides, the transition metal d-orbital hybridizes with the oxygen p-orbital leading to delocalized electrons. However, the d-orbital itself has a local potential due to valence electrons which is a key ingredient for the Mott phase. The Mott insulating state is present in a number of compounds such as such as Ti2O3, V2O3, Cr2O3, MnO, FeO, CoO, NiO, and CuO. Representative resistivity data of various types of MITs [34-36] are shown in Figures 3.6a–3.6c. This theoretical framework, together with tremendous experimental evidence from bulk measurements, have been nicely summarized in the review article by Imada, Fujimori, and Tokura in 1998 [28].



Figure 3.6: Mott insulating states in Transition Metal Oxides (a) BC-MIT in rare-earth nickelates, where the transition temperature increases with increasing atomic numbers (from La to Sm) [9]. (b) FC-MIT in Ca-doped YTiO3, where the materials become metallic for x > 0.3 [10]. (c) CO-MIT in half-doped Nd0.5Sr0.5MnO3, whose low-*T* insulating phase can be driven to metallic by strong magnetic fields [36].

The work mentioned in Figure 3.6 has been done more than two decades ago and since then, strongly correlated oxides have undergone tremendous investigation. In terms of material systems, the epitaxial growth of oxide thin films with atomic layer precision brings a new dimension to the research [37–39]. The effects of different substrates experience different degrees of strain and octahedral tilt/rotation results in the shift of electronic bands and potentially the change of MITs has been investigated [40]. The ability to create oxide hetero-interfaces also leads to quantum confinement and interfacial charge transfer effects, which are not present in bulk materials [41–44]. In particular, the interfacial quality of all-oxide hetero-junctions approach that of traditional III-V semiconductors, it has been demonstrated that many exotic phenomena such as MITs [45], fractional quantum Hall effect [46], superconductivity [47], and multiferroicity [48] can be realized in oxide heterostructures.

Filling factor is an important tunable parameter and electric fields are used as such to investigate MIT [49, 50]. In correlated systems, appreciable changes in MITs usually take place when the doping level is 10% or higher. Such a high degree of substitution inevitably introduces strong disorders or even unwanted clusters in the materials. In recent years, carrier modulation by electrostatic field effect, which exhibits much less disorder effect than chemical doping, has been extensively investigated for correlated materials. Ferroelectrics or ionic liquids as the gate dielectrics, a carrier concentration up to $10^{14} \sim 10^{15}$ cm⁻² can be induced, which is sufficient to modify or even drive the MITs [51–62]. Combined with thin-film technology, it may be possible to study the FC-MIT on one single device with carrier density continuously tuned throughout the phase diagram.

PROBING METAL-INSULATOR TRANSITION

Conventionally, the MITs are mostly studied by measuring macroscopic properties such as resistivity, magnetization, optical reflection/transmission, specific heat, and photoemission spectrum, among others [26]. On the other hand, it has become increasingly clear that, due to the multiple energetically competing orders, mesoscopic electronic inhomogeneity is ubiquitous in strongly correlated materials even far away from the transition [73]. Phase separation is observed in these systems, which if brought under control, can be used for device applications. A local imaging tool would be quite useful to observe the coexistence of these phases and would allow to study the evolution of these phases as a function of an external stimuli such as Temperature, Pressure, Magnetic field, Electric field, Strain, Light etc.

To date, many local probes have been utilized to study the coexisting phases or domains in strongly correlated systems. Representative images [64–67] are shown in Figure 3.7. Here magnetic force microscopy (MFM) measures the local magnetization, near-field scanning optical microscopy (NSOM) probes the local optical conductivity, scanning tunneling microscopy (STM) maps the local density of states, and conductive atomic-force microscopy (C-AFM) detects the local tip-sample current through a Schottky contact. While all the above techniques are capable of visualizing inhomogeneous phases, the key physical parameter during the MITs, which is the local electrical conductivity, is surprisingly difficult to probe by established tools. More importantly, many MITs occur at the buried oxide hetero-junctions or under the gate dielectrics, which presents a challenging task to many surface probes. A new approach to resolve the mesoscopic sub-surface conductivity in a quantitative manner is crucial to



Figure 3.7: Visualizing Phase separation through Scanning Probe Microscopy (a) MFM image of a La_{0.225}Pr_{0.4}Ca_{0.375}MnO₃ single crystal [64]. (b) NSOM image of a VO₂ thin film grown on an Al₂O₃ substrate [65]. (c) STM image of a Pr_xCa_{1-x}Fe₂As₂ (x = 10.5%) single crystal [66]. (d) C-AFM image of a VO₂ thin film grown on a doped-Si substrate [67].

MICROWAVE IMPEDANCE MICROSCOPY FOR CHARACTERIZING PHASE TRANSITIONS

Microwave Impedance Microscopy is a recently established tool to visualize local electrical properties with nanoscale resolution. Here, I would discuss research in the two

families of Transition metal oxide materials which have benefited by being investigated using this technique.

Rare-earth nickelate compounds (RNiO₃, R = La ... Lu) represent a textbook example in that the physical properties can be continuously tuned by structural properties [59, 93]. As shown in Figure 3.8a, bulk RNiO₃ crystals display the MIT (except for R = La whose transition temperature TMI may be pushed down to 0 K) with TMI monotonically increasing with increasing atomic numbers, which correspond to decreasing ionic sizes, decreasing Ni-O-Ni bond angles, and decreasing perovskite tolerance factors [69]. An antiferromagnetic ordering of the magnetic moments also occurs on or below TMI. The insulating phase is usually classified as a charge-transfer insulator with a gap opening between O-2p and Ni-3d orbitals, although recent studies show that charge ordering of the Ni sites can also play an essential role [70, 71]. Despite a long history of investigations, the driving force of the MIT and the exact nature of the ground state are still controversial.



Figure 3.8: MIM investigations on Nickelates (a) Phase diagram of Rare Earth Nickelates (RNiO₃) [69]. (b) Thickness dependence on resistivity for SNNO grown on LAO [81]. (c) Top: Optical image of a Hall-bar-shaped SNNO device (unpublished). The background is amorphous TiO₂. Bottom: MIM-Im images above (left) and below (right) the transition temperature of ~ 180 K within the dashed area in the optical picture.

Before 2000, RNiO3 was mostly studied in the bulk form and the synthesis required very high pressure and temperature. The introduction of pulsed-laser deposition enabled the growth of high quality nickelate thin films under mild conditions, as well as the exciting strain-controlled MITs of films on various substrates [72–78]. Due to the first-order nature of the MIT, coexisting metallic and insulating phases are expected around TMI, whose shape and dimension may carry important information of the strain field. Working with our collaborators (Prof. Xia Hong at University of Nebraska, Lincoln and Prof. Chang-Beom Eom at University of Wisconsin, Madison), we used low temperature MIM setups in our lab to visualize the emergence of inhomogeneous insulating phase in the metallic background as seen in Figure 3.8c acquired at 150 K (unpublished).

The lattice degree of freedom in nickelates can be further explored by looking at the alloys of different RNiO₃ compounds. Sm_{0.5}Nd_{0.5}NiO₃ (SNNO) is of particular interest since it is at the phase boundary where electronic and magnetic orders become decoupled. In addition, the TMI of SNNO is close to room temperature, which is of technological relevance for oxide-based electronic and spintronic devices [79–81]. Figure 3.8b shows the transport data for 2, 3, 4.4, and 18 nm SNNO films on LaAlO3 [81]. Except for the 2-nm film, which is likely due to the electrical 'dead layer' effect, the MIT and hysteretic behavior are evident from the resistivity measurement. The preliminary results in Figure 3.8c clearly display the emergence of insulating phase below the TMI of SNNO (unpublished). Interestingly, it is shown that the density of states is particularly low for SNNO films [81]. In other words, it is possible to deplete the carriers through the established ion-gel gating technique and realize FC-MIT in a typical BC-MIT system. The simultaneous MIM imaging and transport work will shed some light on this important problem in strongly correlated materials. Hole-doped rare-earth manganites ($R_{1-x}A_xMnO_3$) are prototypical correlated systems where charge, spin, lattice, and orbital degrees of freedom are simultaneously active. The research effort here has been largely driven by the colossal magnetoresistance (CMR) effect [83–85]. Figure 3.9 (a) shows the rich phase diagram of $R_{1-x}A_xMnO_3$ [84]. Different correlated states, e.g., Mott insulators, charge ordered insulators, and doubleexchange metals, may occur in RMnO₃. Due to the presence of many competing phases, the materials are very sensitive to external stimuli such as heat, pressure, magnetic field, electric field, and illumination, which can drive the system across the metal-insulator phase boundary. The tendency of phase separation is established both theoretically and experimentally and percolation is believed to be important in these materials [84].



Figure 3.9: MIM investigations on Manganites (a) Phase diagram of R_{1-x}A_xMnO₃ for several pairs of rare-earth elements and dopants [84]. Here A, C, CE, and G refer to various types of anti-ferromagnetic orders. F refers to the ferromagnetic order. (b) MIM-Im images of (left) Nd_{0.5}Sr_{0.5}MnO₃ on (110) SrTiO₃ [87] and (right) Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO₃ thin film on (110) LSAT [86].

Prior MIM work has demonstrated the ability to image electronic inhomogeneity in CMR manganites. The MIM images in Figure 3.9b vividly manifest the phase separation in the 30-nm $Nd_{0.5}Sr_{0.5}MnO_3$ (driven by B) [87] and 40-nm $Pr_{0.55}(Ca_{0.75}Sr_{0.25})_{0.45}MnO_3$ (driven by T) [86] thin films. The orientation order of the emerging phase highlights the strain effect.

SUMMARY

In this section, we went through the basics of band theory and its assumptions and short comings. The explanations provided by the models made by N.F Mott and J. Hubbard to explain those discrepancies has been the foundation of strongly correlated physics. The last two decades has foreseen a lot of progress in understanding these systems. Understanding and controlling Metal-Insulator transitions not only gives insights about the underlying mechanisms and related phenomenon of Superconductivity, Colossal Magnetoresistance, Quantum Criticality, Charge/Orbital ordering, but also has applications to build novel electronic devices. The interplay of charge, orbital, spin and lattice degrees of freedom in strongly correlated systems can easily be studied by direct measurements of the local electronic properties of these systems. In that regard, Microwave Impedance Microscopy has established itself as a non-invasive technique to spatially resolve permittivity and conductivity of a material undergoing a Metal to Mott insulator transition and uncovering key insights about these systems [86,87]. I have used this technique to discover new electronic phases in bilayer doped calcium ruthenates which would be discussed in detail in the next sections.

CHAPTER 4

METAL-INSULATOR PHASE TRANSITION IN BILAYER CALCIUM RUTHENATES

Strongly correlated electron systems are extensively investigated by the condensed matter physics community [89]. Because of the simultaneously active charge, spin, orbital, and lattice degrees of freedom, nanoscale phase separation is widely observed in complex materials. The size, shape, and evolution of these competing phases are largely responsible for many exotic behaviors under external stimuli. On the other hand, as first-order phase transitions are always accompanied by coexisting phases, it remains to see whether new electronic states can develop during the metal-insulator transitions in strongly correlated materials.

INTRODUCTION

The Ruddlesden–Popper series of alkaline-earth ruthenates $(Sr,Ca)_{n+1}Ru_nO_{3n+1}$ display a wealth of fascinating behaviors that are representative of strongly correlated systems [90]. Compared with the Sr-based compounds [91, 92], the metallicity of the Cabased counterparts, if any, is much weaker due to the more distorted crystal structures [90]. For instance, CaRuO₃ $(n = \infty)$ is a paramagnetic 'bad' metal (PM-M) close to the antiferromagnetic (AFM) instability [93], whereas the single-layer (n = 1) Ca₂RuO₄ is a G-type AFM Mott insulator (G-AFM-I) at room temperature and undergoes a metalinsulator transition (MIT) at $T_{MIT} = 357$ K [94]. The intermediate member of bilayer (n =2) Ca₃Ru₂O₇ is more complex, showing a magnetic transition at $T_N = 56$ K and an MIT at $T_{MIT} = 48$ K [95 – 99]. The magnetic ordering below T_N is of A-type AFM, i.e., ferromagnetic bilayers stacked antiferromagnetically along the *c* axis, and the moments switch from the *a* axis (denoted as AFM-*a*) to the *b* axis (AFM-*b*) upon cooling, as illustrated in Figure 4.1b [99]. Moreover, the small Fermi pocket in the AFM-*a/b* phases [100] is suppressed by isovalent Ti doping into the Ru site through bandwidth reduction, which drives the ground state of $Ca_3(Ru_{1-x}Ti_x)_2O_7$ into G-AFM-I beyond x = 3% [101 – 106]. Such simultaneously active lattice, charge, and spin degrees of freedom make Ti-doped $Ca_3Ru_2O_7$ an ideal testbed to explore the correlation physics in complex oxides.



Figure 4.1: a) The phase diagram for Ti-doped bilayer Calcium ruthenates. [104]



b) Schematics of the magnetic structures of (from left to right) G-AFM, AFM-*a*, AFM-*b*, and PM phases [99, 101]. Only the RuO₆ octahedrons are shown here for clarity.

The multiple phases in Ca₃(Ru_{1-x}Ti_x)₂O₇ with distinct electrical and magnetic properties (Figure 4.1a) are analogous to the colossal magnetoresistive (CMR) manganites [107]. As in any first-order phase transitions, the MIT in most CMR systems is accompanied by a mixture of two terminal phases, which underlies the drastic change of resistivity under external stimuli such as temperature (*T*), magnetic (*B*) field, electric current, light, and pressure [108].

In this Chapter, we report the direct visualization of coexisting phases across the Mott transition in 10% Ti-doped bilayer calcium ruthenates using near-field microwave microscopy. Surprisingly, within a narrow range of T and B-field near the transition, stripe-like metallic domains oriented along the a-axis, which differ from the two terminal

phases, appear inside both the G-AFM-I and PM-M regions. Based on the dynamic emergence of the mesoscopic phases and fine features in the macroscopic transport and magnetization data, a phase diagram that includes the phase coexistence can be constructed. Our observation of orientation-ordered phase separation suggests that strongly correlated materials with 4*d* electrons share certain common aspects, while differ in others, with the 3*d* correlated electron systems.

EXPERIMENTAL TECHNIQUES

Single crystals $Ca_3(Ru_{0.9}Ti_{0.1})_2O_7$ in this study were grown by the floating zone technique [101].

In order to explore the real-space evolution of this complex phase transition, we carried out cryogenic microwave impedance microscopy (MIM) [110], as illustrated in Figure 4.2. The 1 GHz signal is delivered to a tungsten tip (diameter ~ 100 nm) glued to a quartz tuning fork (TF) for topographic feedback [9, 15]. The microwave electronics measure the real (MIM-Re) and imaginary (MIM-Im) parts of the tip-sample admittance, which is demodulated at the TF resonant frequency (~ 40 kHz) to form the corresponding AC_MIM images [15].



Figure 4.2: Schematic of the tuning-fork-based cryogenic MIM setup. The TF electronics control the z-scanner and provide the reference to demodulate the MIM signals.

TRANSPORT MEASUREMENTS:

The *T*-dependent magnetic susceptibility (χ) and in-plane resistivity (ρ_{ab}) data with relatively coarse steps (0.05 K for χ and 0.5 K for ρ_{ab}) are plotted in the insets of Figure 4.3a and 4.3b, respectively, showing a single transition from G-AFM-I to PM-M at ~ 113 K upon warming. The results appear to agree with prior investigations on the same x = 10% material, where no intermediate states between the two phases were found [102, 104]. The situation, however, was different when much finer measurements were taken (0.01 K step for χ and 0.1 K for ρ_{ab}), as shown in Figures 4.3. In the $\chi(T)$ curve, several jumps characteristic for meta-magnetic transitions were observed. Within a narrow window in the resistivity data, $\rho_{ab}(T)$ is lower than that of the PM-M phase, reminiscent of the parent compound where the metallic AFM-*a/b* phase develops [95, 99].



Figure 4.3: Transport measurements on $Ca_3(Ru_{0.9}Ti_{0.1})_2O_7$ (a)Magnetic susceptibility taken under an out-of-plane field of 1000 Oe, showing multiple metamagnetic steps around the transition. The inset shows χ (T) in a wider temperature range and coarse steps, where only a single transition is observed. (b) In-plane resistivity taken at Bc = 0 T and 9 T. The inset shows χ ab(T) at 0 T in a wider temperature range and coarse steps.



Figure 4.4: Magnetoresistivity at various temperatures. The field sweep direction is indicated for the 112.6 K data.

Figures 4.3 and 4.4 also show the result under an out-of-plane *B*-field, which is compatible with our scanning experiment. It should be noted that the spin flip-flop transition for *B* // *c*-axis occurs at much higher fields than *B* // *a*- or *b*-axis and intermediate states are present throughout the transition [109]. As a result, the effect of *B*_c in this work is mostly to destroy the G-AFM ordering. The presence of multiple steps and sudden jumps in the magnetoresistance data indicates that the MIT may involve richer physics than previously conjectured. In particular, the resistivity at 113.2 K jumps between $2 \times 10^{-3} \Omega \cdot cm$ (PM-M) and a lower value of $4 \times 10^{-4} \Omega \cdot cm$, indicative of the emergence of a new metallic phase near the transition.

MIM MEASUREMENTS AND OBSERVATIONS:



Figure 4.5: MIM measurements (a) Simulated AC_MIM signals as a function of ρ_{ab}. The resistivity values of relevant phases are indicated in the plot. (b) Topographic images at three selected temperatures. Note that the color scale corresponds to relative height difference within each frame. The inset shows a line profile in the 114.72 K image. (c) AC_MIM-Re images at various temperatures across the transition. Phases I to IV are labeled in the images. The blue ellipses in the 114.64 K and 114.72 K images show the dynamic appearance and disappearance of two stripes. The scanning directions (x and y) and the crystalline axes (a and b) are indicated in the bottom left and top right corners, respectively. All images are 20 µm x 20 µm.

Figure 4.5a shows the simulated AC_MIM-Im/Re signals as a function of the inplane resistivity (Figure 4.8, [113]), taking into the fact that $\rho_{ab} \ll \rho_c$ in this material [104, 105]. Even though the low-*T* phase is insulating, its resistivity near the MIT is still on the conductive side for the 1 GHz MIM [15]. On this side of the response curve, it is easier to distinguish the PM-M and G-AFM-I regions in the MIM-Re channel, where the signal decreases as the sample becomes more conductive, due to the cleaner data and less topographic crosstalk than MIM-Im. In addition, surface particles observed in the topography (Figure 4.5b) also display vanishing MIM-Re signals. Nevertheless, they are clearly on the resistive side of Figure 4.5a as their MIM-Im signals are the lowest in the map (Figure 4.8 (a), [113]).

The AC_MIM-Re images at various temperatures across the MIT are shown in Figure 4.5c (complete data in Figure 4.9, [113]). Note that the apparent $T_{\rm MIT}$ in Figure. 4.3 - 4.5 may differ slightly by a few Kelvins, depending on the detailed thermal or magnetic-field history of the sample, which is not uncommon for strongly correlated materials. For temperatures much below $T_{\rm MIT}$, the sample was mostly in the insulating state (Phase I), with some highly conductive areas (Phase II) observed in the microwave image. Since T_{MIT} decreases as decreasing Ti-doping, Phase II is likely associated with local deficiency of Ti concentration, which segregate into isolated regions during the floating-zone crystal growth. Since the lattice constant sensitively depends on the Ti doping, such minority phases may self-organize in regular shapes under strain when the crystal is cooled to room temperature, which could explain its ribbon-like shape and orientation along the high-symmetry [110] and [1-10] directions. Finally, we note that Phase II does not exhibit obvious topographic features throughout the phase transition (Figure 4.5b). As the *c*-axis lattice constant is rather different between G-AFM-I and PM-M phases [101, 105], Phase II regions in the MIM images must be thin slabs on the surface. One cannot, however, exclude the existence of similar Ti-deficient domains in the interior of the sample.

Starting from 114.04 K, metallic stripes (Phase III) were observed in the MIM images, whose length and areal density grew rapidly with increasing *T* at 0.1 K steps. The stripes are oriented along the *a*-axis of the crystal, as determined by the X-ray diffraction (XRD) data (Figure 4.10, [113]). The width of the stripes ranges from 100 nm (limited by the spatial resolution) to ~ 1 μ m and the spacing between adjacent ones is 3 ~ 5 μ m. The micrometer-sized separation between the stripes indicates that the elastic strain between different phases, rather than the electronic correlation, plays a key role here. In particular, the characteristic spacing is likely determined by the length scale at which the strain can be accommodated inside the crystal.

The appearance of stripes is dynamic (blue ovals in Figure 4.5c) and they are not pinned to specific locations in different thermal cycles (Figure 4.11, [113]). At 114.72 K, another metallic phase (Phase IV) set in, which quickly swept through the scanned area with an additional ~ 0.3 K. The topographical images in Figure 4.5b indicate that Phase IV is associated with a pronounced increase in height, corresponding to the ~ 0.1% increase of lattice constant in the *c*-axis across the MIT [101, 105]. Phase IV is thus the global PM-M phase that extends through the entire crystal.

Since the MIM contrast between the two possible metallic phases (PM-M and AFM-a/b) is too small, it is not obvious from Figure 4.5(c) whether Phase III is the same as II/IV or represents a new electronic state. To enhance the contrast, we have used a blunter tip in a different cool down [113].


MIM MEASUREMENTS WITH MAGNETIC FIELD VARIATION:

Figure 4.6: MIM measurements with Magnetic field (a)Topographic and AC_MIM-Re images at 111.40 K and 0 T of a different cool down. (b) MIM images at various temperatures and 0 T. (c) MIM images at various magnetic fields and 111.40 K, except for the last image at a higher temperature and 4 T. Phases I to IV are again labeled in the data. All images are 15 micron by 15 micron. (d) Line profile in (c), showing the AC_MIM-Re signals across stripes in both the G-AFM-I and PM-M phases.

Figure 4.6a shows the topography and AC_MIM-Re images at T = 111.40 K and B = 0 T, from which two rounds of experiments were performed. In Figure 4.6b, the *B*-field was kept at zero during a warm-up across the transition. Similar to Figure 4.5c, all four phases – I as G-AFM-I, II as local PM-M at lower *x*, III as the stripes, and IV as the global PM-M – were observed in this area. Strikingly, the stripes could also be seen inside Phase IV. The same phenomenon was also observed in Figure 4.6c, where we kept

T = 111.40 K and ramped up the *B*-field, except for the last image (Figure 4.12, [113]). Moreover, the line profile in Figure 4.6d shows that the stripe domains inside Phases I and IV display the same MIM signals. In other words, the stripes are indeed a new electronic state that is distinct from the two terminal phases of the transition.

To our knowledge, this is the first observation of an additional phase during the metal-insulator transition in strongly correlated materials, highlighting the complexity in 4*d*-ruthenates. Interestingly, the stripes in the two major phases seem to avoid each other at the boundary (Figure 4.13, [113]). Based on the prior knowledge in Ca₃(Ru_{1-x}Ti_x)₂O₇ [101 – 106], the stripes are likely the sequential appearance of AFM-*a* and AFM-*b* phases during the transition, although we do not have direct evidence on their magnetic ordering. Besides, Phase III does not exhibit appreciable topographic contrast over the G-AFM-I or PM-M phases, whose lattice constants in the *c*-axis differ by ~ 0.1% [101, 105]. Since the noise floor of our TF feedback is 2 ~ 3 nm, one can infer that the stripes in the MIM images are surface features with a thickness no more than a few microns. Similar to the analysis of Phase II, however, we cannot exclude the appearance of such domains inside the crystal.

MODIFIED PHASE DIAGRAM:



Figure 4.7: Modified phase diagram (a) Magnetotransport curve at T = 112.6 K divided into four sections based on sudden changes of the signals. (b) Phase diagram in a narrow temperature and field range taking into account the phase separation. The squares, circles, and triangles (open, solid, crossed from $\rho(T)$, $\rho(B)$, and $\chi(T)$, respectively) mark the three phase boundaries indicated in the graph. For consistency, all data points are measured on the insulator-to-metal part of the hysteresis loop, i.e., warming up for Tdependence and ramping up for B-dependence.

The mesoscopic MIM imaging allows us to reevaluate the magnetization and transport data and construct a new phase diagram for Ca₃(Ru_{0.9}Ti_{0.1})₂O₇ [102, 104, 114] that includes the nanoscale phase separation. For instance, the magnetotransport curve at 112.6 K (Figure 4.7a) can be divided into four sections based on sudden changes of the slope, presumably due to the appearance or disappearance of certain coexisting phases. Similar analysis can be applied to the $\rho(T)$ and $\chi(T)$ data in Figure 4.2. As shown in Figure. 4.7b, the coexistence of the stripe phase with the two terminal phases reveals a complex energy landscape that takes place near the Mott transition in this system.

Subtle difference is also expected between different members in the Ruddlesden– Popper series. For instance, stripe domains that are the same metallic phase at the end of the insulator-to-metal transition were also reported in Ca_2RuO_4 [124], which occur near the physical boundary between the two competing phases. In our case, the stripes, which differ from the two terminal states of the Mott transition, are not confined to the interface between the two global phases. In fact, the effect of phase separation is observable in macroscopic measurements. This new complexity is likely due to the fact that more energetically competing phases are available in the bilayer than single layer ruthenates.

FINITE-ELEMENT ANALYSIS OF THE AC_MIM SIGNALS



Figure 4.8: Simulation curves for different tip widths (a) Simulated AC_MIM signals as a function of the in-plane resistivity for a sharp tip. (b) Simulated AC_MIM-Re signals for sharp and blunt tips. The dc resistivity values of the PM-M and stripe phases are indicated in the plot. (c) Simulated 1 GHz quasi-static potential distribution around two tips for $\rho_{ab} = 10^{-3} \Omega \cdot cm$.

To understand the AC_MIM signals, we performed finite-element analysis (FEA) to calculate the tip-sample admittance, as shown in Figure 4.8a. Here we first computed the approaching curve towards the sample surface, followed by demodulation of AC_MIM-Im/Re signals for a sinusoidal tapping of the tip (amplitude ~ 15 nm in this work). Detailed simulation procedure can be found in Ref 126. To avoid the divergence of the signals as the tip is in contact with a metallic sample, we assume that the minimal

tip-sample spacing is 1 nm. Note that $Ca_3(Ru_{1-x}Ti_x)_2O_7$ is highly anisotropic between the in-plane and out-of-plane directions [127]. We assume that $\rho_c = 100 \rho_{ab}$ in the FEA modeling.

The MIM signals are very sensitive to the exact tip conditions in the experiment. It is possible that the tip used to take the images in Figure 4.6 shown previously is blunter than that in Figure 4.5. As shown in Figure 4.8b, while a sharp tip (semispherical apex with 100 nm radius) cannot differentiate the PM-M and stripes, a very blunt tip (flat end with 100 nm radius) gives much higher contrast between the two phases.

We acknowledge that this effect alone cannot quantitatively explain all features in the data, such as the comparable contrast between G-AFM-I and PM-M phases in Figures 4.4 and 4.5. Given the many approximations in the FEA modeling (1 nm minimum tip-sample spacing, $\rho_c = 100 \rho_{ab}$, same conductivity at dc and GHz...), we believe our simulation provides a semi-quantitative framework for the data interpretation. The conclusion that three phases (G-AFM-I, stripe, and PM-M) are observed during the Mott transition is not affected by the simulation result.

COMPLETE SET OF T-DEPENDENT DATA





Figure 4.9: Complete set of the *T*-dependent topography and AC_MIM-Im/Re images.

The complete topography and AC_MIM images in Figure 4.5 discussed previously are shown in Figure 4.9. The signals in the Re channel are generally cleaner due to the higher contrast and less topographic crosstalk. Since AC_MIM-Re signals on the conductive side of the response curve (see Figure 4.8) are decreasing as increasing sample conductivity, we flip the color scale in the data. The surface particles appear as dark spots in AC_MIM-Im, suggesting that they are not conductive.

In the MIM images, one can also observe a few conductive stripe-like features along the [1-10] direction well below the Mott transition temperature, which are more pronounced in the MIM-Im channel than the MIM-Re data. Similar behaviors are seen in other areas during our experiment. In all, the slab-like features along the [110] and [1-10] directions are Ti-deficient domains (Phase II) and the stripe-like features along the *a* axis are the emergent AFM-a/b phase (Phase III).

Similar analysis also applies for Phase III. In general, the resistivity measured in transport experiments is a bulk property. However, the bilayer CaRuO-327 system is strongly quasi-2D with $\rho_c/\rho_{ab} \sim 10^3$ near the Mott transition. In other words, for the sample with a thickness of 100 ~ 200 µm in this study (see Figure 4.10 for a picture of the crystal), a surface layer of 1 µm in height could dominate the in-plane transport. We nevertheless recognize that the MIM only has a probing depth comparable to the tip diameter, i.e., on the order of 100 nm. As a result, one cannot exclude the possibility that such AFM-*a/b* domains also occur in the interior of the crystal.

DETERMINE CRYSTAL ORIENTATION BY X-RAY DIFFRACTION



Figure 4.10: Laue diffraction measurements (a) Picture of the Ti-doped Ca₃Ru₂O₇ crystal mounted on the MIM sample holder. The scan directions (*x*-axis parallel to the copper strip) are labeled in the photo. Note that the *x* and *y* axes of the MIM image in the inset are rotated from that in the main text. The scanned area is roughly inside the orange dashed circle indicated by the arrow. (b) Laue X-ray diffraction pattern (black spots) overlaid on the calculated pattern (red dots) using the lattice constants of Ca₃(Ru_{0.9}Ti_{0.1})₂O₇, where the *a* and *b* axes are oriented along the directions labeled in (a). (c) Same as (b) except that *a* and *b* axes are swapped for the calculated pattern (red dots). The results inside the blue dash-dotted circles show much better agreement between the measured and simulated patterns in (b) than that in (c).

In order to determine the orientation of the stripe phase, we performed careful Laue X-ray diffraction (XRD) experiment and analysis. Figure 4.10 (a) shows the $Ca_3(Ru_{0.9}Ti_{0.1})_2O_7$ crystal mounted on the MIM sample holder, where the slow scan direction (*x*) is parallel to the copper strip. We then took the crystal for high-resolution XRD measurement and determined the two principle in-plane axes. Note that the in-plane lattice constants of $Ca_3(Ru_{0.9}Ti_{0.1})_2O_7$ differ by ~ 2% between the two axes [102]. As shown in Figure 4.10 (b), the calculated XRD pattern (red dots) matches nicely to the experimental data (black dots) if we orient the *a* and *b* axes according to the labels in Figure 4.10 (a), whereas swapping the assignment for these two axes in Figure 4.10 (c) leads to poor fit to the measured results. The good fitting to the XRD data in Figure 4.10

(b) also indicates that the crystal does not contain a lot of twinned domains within the X-ray spot size of ~ 1 mm. We can therefore safely assume that the crystalline orientation in the MIM images follows that in Figure 4.10 (a).

POSITION OF STRIPES AT DIFFERENT COOL DOWN



Figure 4.11: AC_MIM-Re images around the same area for three different rounds of experiment. The stripes observed in the first two rounds are indicated in the last image by green and blue dashed lines.

The metallic stripe domains emerged during the Mott transition are not always pinned to specific locations. Figure 4.11 shows the AC_MIM-Re images around the same area at three different rounds of cool-down. We overlay the stripes observed in the first two images (green and blue dashed lines) onto the last image, which is the 114.64 K data in Figure 4.5. It is obvious that some stripes appear at different locations from cool-down to cool-down, suggesting that such competing state emerges dynamically rather than being pinned by local disorders.

The data in Figure 4.11 also illustrate that different thermal history can lead to different apparent T_{MIT} in our experiment. For the Round 3 data, the sample was cooled to ~ 10 K and slowly warmed up through the transition. On the other hand, when we

cooled the sample to 100 K and rapidly warmed it to 109 K before slow scans, the stripes started to appear at lower temperatures, i.e., 109.45 K in Round 1 and 109.35 K in Round 2. Note that these images are comparable to the 114.03 K data in Figure 4.5. As a result, a single T_{MIT} does not apply for this complex system and the transition strongly depends on the thermal/field history.



FIELD-DEPENDENT MIM DATA AT A SLIGHTLY HIGHER TEMPERATURE

Figure 4.12: Complete set of *B*-dependent images at 112.15 K. All images are 15 μ m × 15 μ m.

The last MIM image in Figure 4.5 of the main text was not taken at the same temperature as others since the magnet was on the verge of quenching. Instead, we took another set of images at a slightly temperature of 112.15 K than that in Figure 4.5 (111.40 K). At this temperature, the zero-field image was comparable to the 6.4 T data at 111.40 K. As a result, we were able to use lower fields to observe the evolution of stripes (appearing at low fields and eventually disappearing at high fields) within the PM-M

phase, as displayed in Figure 4.12. Other features, such as the surface particles in topographic and AC_MIM-Im images, are similar to the data shown earlier.

The fact that the apparent T_{MIT} differs by a few Kelvins in our data is worth some discussions. For MITs in strongly correlated materials, it is not uncommon that the transition depends on the detailed thermal or magnetic-field history of the sample. In particular, the images in Figure 4.5 were taken when the sample was cooled to the base temperature of ~ 10 K and then gradually warmed up to cross the phase transition. For the data in Figure 4.6, the sample was only cooled to slightly below 100 K before warming back towards the transition. The fact that we ramped up and down the magnetic fields when taking Figure 4.6 and Figure 4.12 may have also played a role. As a result, it is not surprising that the apparent T_{MIT} differs by a few Kelvins (113 ~ 114 K in Figure 4.3, 114 ~ 115 K in Figure 4.5, 112 ~ 113 K in Figure 4.6) in our experiment.

STRIPES NEAR THE PHYSICAL BOUNDARY BETWEEN G-AFM-I AND PM-M PHASES

T = 111.40 K



Figure 4.13: *B*-dependent MIM images using a different false-color scale. All images are $15 \ \mu m \times 15 \ \mu m$.

Some MIM images in Figure 4.6 are replotted in Figure 4.13 with a different false-color scale such that the stripes are more visible near the physical boundary between G-AFM-I and PM-M phases. Several key features are observed inside the green ellipses in each image. First, the metallic stripes are not confined to the interface between the two global phases, nor are they parallel or perpendicular to the interface. The situation is different from that in the current-driven Mott transition in Ca₂RuO₄, where the stripes

appear near the physical boundary between the two global phases [124]. Secondly, the stripes are not continuous across the boundary, e.g., they simply terminate within the PM-M domain in the 6.5 T and 6.7 T images. Finally, for B = 6.9 T, the stripe in the PM-M domain bends itself to avoid the connection with the stripe in the G-AFM-I domain. Future theoretical work that takes into account the elastic strain energy may be needed to explain such phenomena.

CONCLUSION

As a concluding remark, it is instructive to compare our results with nanoscale phase separation in other complex oxides. In the more extensively studied 3*d* correlated electron systems near MITs, the coexisting phases may exhibit random shapes and sizes [115 - 119] or orientation-ordered patterns [120 - 123]. The latter clearly signifies the strong effect of elastic strain on phase transitions. For comparison, stripe-like competing phases are commonly seen in single crystals of 4*d* ruthenate perovskites, such as Ca_2RuO_4 [124], Mn-doped $Sr_3Ru_2O_7$ [125], and now $Ca_3(Ru_{1-x}Ti_x)_2O_7$. It is possible that, as the on-site Coulomb energy is reduced for the more extended 4*d* orbitals with respect to the 3*d* counterpart, the lattice degree of freedom in ruthenates becomes prominent for bulk ruthenates materials.

In summary, we report the nanoscale microwave imaging on doped $Ca_3(Ru_{1-x}Ti_x)_2O_7$ through the simultaneous insulator-to-metal and antiferromagnetic-toparamagnetic transition. Different from the previous picture that a single-step process takes place, we observed a stripe-like metallic phase within a narrow temperature and field range of the transition, which is in a different electronic state from the two majority phases. The emergence of such orientation-ordered domains is consistent with the macroscopic transport and magnetization data, suggesting the strong interplay between electronic and lattice degrees of freedom in 4*d* correlated electron systems.

CHAPTER 5

METAL-INSULATOR TRANSITION IN MN DOPED BILAYER CALCIUM RUTHENATES

It has been demonstrated that a tiny amount of chemical doping can induce a Metal-Insulator Phase transition in bilayer calcium ruthenates. Various investigations have been carried out by doping the parent bilayer compound with a wide variety of dopants, Particularly Fe, Cu, Mn, Co, Cr and Ni [106]. However, the effect of the dopant ion on the nature of the newly discovered stripe-phase remains unknown. The dopants can be classified into two categories: - Magnetic (Cr, Fe, Ni, Co, Mn [111]) and Non-Magnetic (Ti). In Ti doped parent compound, we have shown that a perpendicular magnetic field can be used to destroy the G type AFM ordering and causes the MIT transition temperature to decrease. However, a magnetic dopant would add more complexity to the system. Hence, a natural next step would be to visualize the coexisting phases in the bilayer calcium ruthenate which is chemically doped with a magnetic ion.

ROLE OF 3D DOPANTS

To understand the role of a dopant, we need to start by looking at the simplest picture of Mott insulating state in a Transition Metal Oxide. In an octahedron constructed using a Transition metal ion surrounded by six oxygen atoms. The ion usually has a d₁, d₂, d₄, or d₅ configuration.



Figure 5.1: Various d orbital filling levels for Transition Metal oxides.

Since the orbitals are partially occupied, the system should be metallic. However, we know that there are many Transition Metal Oxide compounds with these configurations which are Mott insulators. If the t_{2g} orbital degeneracy is lifted, the system can be in a Mott Insulating state and this degeneracy can be induced by a structural transition which is often accompanied by a magnetic transition. This leads to a high temperature metallic to low temperature Mott Phase transition.

The oxidation state for the Ti dopants is 4+ which is equivalent to the Ru ion while Mn is in mix valent 3+ and 4+ state. Ti⁴⁺ has fully empty 3d orbitals, and Mn⁴⁺ has fully empty spin-down t_{2g} orbitals and fully occupied spin-up t_{2g} orbitals. Since the Ru⁴⁺ 4d states lies at the Fermi level of the system, the parent compound Ca₃Ru₂O₇ is metallic. The energy mismatch between the 3d orbital states and the fermi level in Mn and Ti dopants cause them to act as strong scattering center. This also leads to strong structural distortions. If we look at some other dopant such as Fe⁴⁺, the energy mismatch is much smaller and leads to weaker scattering. Hence, A 3d dopant could act as a strong scattering center which can enhance the low temperature Mott Phase or even a new competing phase could be introduced.



Figure 5.2: The relative crystal-field-split energy levels of Ru, Mn, and Ti ions for $Ca_3(Ru_{1-x}M_x)_2O_7$ (M = Mn or Ti) system [106]

DFT calculations [112,122], have shown that Mn⁴⁺ and Ti⁴⁺ ions can act as a strong scattering centers. The mechanism is a due to the high potential barrier generated in each of these ions which act as a scattering site. This was likely due to the highly localized nature of the 3d⁰ or 3d³ configuration. Figure 5.2 shows that for each Mn4+ ion, there are three 3d electrons occupying the t2g spin-up subband, hence giving it a magnetic nature. Adding additional electron, satisfying Hund's rule, would need to occupy a much higher energy level which is the t2g spin-down subband being above Fermi Level. [125]. Similarly, for Ti-doped samples, if we put another electron it will go to the t2g subband, which is also above the Fermi level according, thus causing the energy to increase. Hence these sites act as a strong scattering center. The scattering effects have also been observed via scanning tunneling microscope (STM) measurements, such as the Freidel-like oscillations in Ti-doped Sr₂RuO₄ [127] and the local DOS (LDOS) modulations and quasiparticle interference effects in lightly Ti-doped $Sr_3Ru_2O_7$ [105]. These unique strong scattering sites with $3d^0$ and $3d^3$ modify the local electron cloud configuration. This leads to a structural distortion which could go beyond local variations [102]. Hence it results in a strong correlation between the lattice and electronic degrees of freedom.

Transport measurements with various dopants in bilayer calcium ruthenate parent compound [106] have shown that only Ti and Mn ions induce a Mott transition with a G type Antiferromagnetic Insulating Phase. Other ions such as Fe are unable to push the system to the transition and remain in a combination of the low temp AFM-b phase and an incommensurate (IC) phase that is characterized by a cycloidal spiral spin structure [125].

TRANSPORT MEASUREMENTS ON MN DOPED BILAYER RUTHENATE



Figure 5.3: In-plane Resistivity measurements on 8% Mn doped bilayer Calcium Ruthenate.

Figure 5.3 shows resistivity measurements on Mn doped Ca₃Ru₂O₇. A level of 4% Mn doping or more drives the system to a G type AFM ordering which is Mott insulating in nature. The doping effects ae very similar to Ti doped sample. However, it is worth mentioning that only Ti and Mn doped samples can induce Mott transitions. However, In the Mn doped sample we do not see any peculiar features in resistivity measurements, particularly the dip in resistivity before the sample undergoes a Metal to Insulator transition. The change in resistivity lies within the sensitivity window of MIM and hence an investigation similar to the Ti doped sample can be performed on this sample.

LAUE X-RAY DIFFRACTION MEASUREMENTS AND TWINNING OF THE CRYSTAL.

Before we begin with the cryogenic MIM scanning, we carefully gathered Laue X-ray diffraction (XRD) measurements. Our experience with the Ti doped sample suggests that in the event we see stripe shaped patterns near the MIT phase transition, they would likely be aligned along one of the crystallographic axis. Hence, orienting the

sample in the optimal manner before attaching it to the sample holder can be achieved by gaining information about the direction of the crystallographic axis. The single crystals were grown using the floating zone technique.

The Figure 5.4 (a) shows the Laue XRD pattern. Note that there is a shadow around each spot. This indicates twinning in the crystal. The parabolic line around the bottom indicates another twinned domain. The calculated XRD pattern is overlaid on the data as shown in 5.4 (b) but due to the twinning of the crystal and the relatively large spot size (mm²) compared to the size of twinned domains, we cannot predict the direction of a and b crystallographic axis of the crystal in our scan area (μ m²). Hence, we have to deal with a uncertainty in the direction of each individual axis but since the twinning only rotates the axis by 90 degrees, we can say that they are definitely aligned along the directions shown in the figure.



Figure 5.4: Laue diffraction measurements (a) Laue X-ray diffraction (XRD) pattern on 8% Mn doped Ca₃Ru₂O₇ single crystal. (b) Calculated XRD pattern overlaid on the experimental observations. (c) Picture of the single crystal sample with orientation of the crystallographic axis derived from the Laue measurement data. Red circle indicating the X-ray spot size used for the measurement and roughly indicates the intended scan area.

The highly twinned nature of the crystal is not preferable as it adds another factor that might affect the orientation of the stripes. We have demonstrated that in the Ti doped sample, the stripe phase and the crystallographic axis have a strong correlation. A low twinned crystal would result in a straightforward analysis, but it remains to see how the stripe phase would behave in a highly twinned crystal where the strain field would vary differently in the twin domains. Hence, we cannot assume the orientation of the stripe phase with respect to the crystallographic axis.



CRYOGENIC MIM SCANS.

Figure 5.5: MIM measurements (a) Topographic image at 67 K. The scan area is relatively flat with three particles which can be used as a reference. (b) MIM real part images describing the evolution of the MIT Phase transition with temperature. The direction of the crystalline axis is depicted in the top right corner. All images are 12 μ m × 12 μ m.

We explore the real space evolution of the Metal-Insulator Phase transition with our cryogenic Microwave Impedance Microscopy setup. We repeat the same procedure we followed for the Ti doped samples. Figure 5.5(a) shows the topographic image which looks relatively flat. The three particles on the top right of the image can be used as a reference point. Since we are studying the temperature evolution, there could be a significant drift in the scan area pertaining to the fact that there could be expansion or contraction of the probe holder, sample holder and the piezo stack with varying temperature. Since these are made of different materials, we observed drift of about a few microns for full cycle of scans. Therefore, it is necessary to have a set of surface particles that can be used as a reference as they are fixed in position. The scan area was observed to be flat however it is worth noting that the topographic noise in our scans was about 5nm. This topographic noise could couple with the MIM signals, especially the Imaginary channel as it is proportional to the capacitance part of the tip sample interaction. However, the change in resistivity is quite large and the change in MIM contrast generates a signal to noise ratio large enough to unambiguously interpret our images and form a qualitative understanding of the Phase transition. The MIM Re channel images have relatively less topographic cross talk and hence can be used to generate clearer images.

Figure 5.5(b) shows various scans with varying temperature. A notable characteristic of a first order first transition is the hysteresis in resistivity. The observed MIT temperature is much higher than our transport data, since it's measurement done during the warm up phase of the cycle. The apparent T_{MIT} will also differ by a few kelvins depending on the thermal history of the sample which is quite common in this class of strongly correlated materials. The low temperature phase is the G-type AFM Insulating phase like what we observed in the Ti doped sample. The diagonal bright regions are conducting domains which remain unchanged in position and can be observed as long as the background is in the dark insulating phase. Low-level of Mn doping in these regions could result in the behavior of this region similar to the parent compound where the condition to satisfy the minimum amount of doping required to transition to the

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Mott phase is not met. These regions could also be used as markers for our scans. The three particles in the upper right corner also appear bright in our scans. The signal strength in the MIM-Re channel for extremely conducting or insulating regions is almost equal, hence these insulating particles appear to have the same signal strength as the conducting regions. MIM-Img channel can be analyzed to remove any ambiguity about the conductivity of these particles. The floating zone growth process for these crystals could lead to an inhomogeneity in the doping concentration, justifying the presence of these regions.

POSITION OF STRIPES AT DIFFERENT COOL DOWN



MIM -Img

Figure 5.6: MIM-Img channel images of the stripes around the same can area but during two different cycles. The measurement is done at 72.75K for both scans.

As we approach closer to the apparent T_{MIT} we observe the much-anticipated stripe phase. The stripes are more evenly spaced and are about 10 microns away from each other, indicating a much larger periodicity compared to the Ti counterpart sample. The large periodicity demonstrates that elastic strain is the key factor rather than electronic correlation. But its width remains about 100-200 nm whose measurement is limited by our spatial resolution. A striking observation would be the orientation of these stripes which are now orientated about 45 degrees from a/b axis, which is a rather very important distinction compared to our previous observations. As we drive the sample through the phase transition to the conducting phase, the stripes start to widen. The width increases gradually over a few kelvins but a tipping point is noticed when a smaller step size in temperature could result in the sudden increase of its width. Eventually, these stripes become large enough to merge with other stripes and encompass the entire sample resulting in the PM-Metallic terminal phase at higher temperatures. Figure 5.6 shows the MIM scans of the stripes when they have about a few microns in width. These images were taken at different warm up cycles and demonstrate that theses stripes are not pinned to a particular location. The emergence of these stripes is not correlated to any kind of underlying inhomogeneity of the region.

COMPARISON OF THE MIT CHARACTERISTICS WITH DIFFERENT DOPANTS.

Our investigation of the Metal-Insulator transition Mn doped Bilayer Calcium Ruthenates has raised more questions than answers. We observe striking differences in the MIT characteristics between the Ti and Mn doped samples. Some differences were expected when we compared the transport measurement such as the noticeable dip before MIT in Ti doped sample is absent in Mn samples. The T_{MIT} for Mn doped samples is much lower than for the Ti doped samples.

MIT characteristics	Mn doped	Ti doped
Stripe Orientation	45 deg from a/b axis (Highly twinned crystal)	Parallel to a axis. (Low twinned crystal)
Evolution of coexisting phases	Widening of metallic stripes	Increasing number of metallic stripes
Phase of stripes	Same as high temperature metallic phase	Different from the high temperature metallic phase (More conducting)
Transition temperature width	3-5K	0.3-0.5K

Table 5.1:Comparison of the characteristics of the Metal-Insulator transition in 8% Mn
and 10% Ti doped Ca₃Ru₂O₇.

As observed earlier, the MIT in these samples is accompanied by a structural change. There is noticeable elongation along the c-axis and flattening along the b-axis which leads to different strain fields across the terminal phases. The observed difference in the T_{MIT} can be attributed to different c/\sqrt{ab} which follows a linear trend for different dopants [106]. A smaller c/\sqrt{ab} in Mn doped samples compared to Ti doped samples leads to lower T_{MIT}. The transition is more gradual in Mn doped samples occurring in a

wider range of 2-4K compared to 0.2-0.5K in Ti doped samples. A larger change in the lattice parameters in the Ti doped samples could imply a more abrupt MIT transition.

The most peculiar characteristic of the phase separation is the emergence of Stripe-like metallic domains which are present in both systems, but their characteristics differ vastly. The orientation of the stripes in the Ti doped sample is parallel to the a axis. The orientation of these stripes is a result of the elastic energy minimization taking into account the structural distortion, particularly the change in b and c lattice constants of the Ruthenium octahedral [126]. For the Mn doped sample, the orientation of the stripes is approximately halfway along the a and b axis. This could either be the result of the nature of the dopant or could be the level of twinning in the crystal. The observed level of twinning is definitely higher in our Mn doped sample. Considering that the Mn and Ti dopants act as strong scattering centers which modify the local electron cloud configuration, thus resulting in local structural distortion. The strain field leads the local structural distortion to extend to the whole structure [128]. Also, the level of twinning and the resulting orthogonal strain fields in twin domains could contribute to make the observed orientation of the stripe phase as the most energetically favorable one.

However, our current understanding of these systems does not explain the difference in evolution. In the Ti-doped sample, we observe the increase in the number of stripes as we drive the system across the phase transition, while in the Mn-doped sample, the stripes start to widen once they appear until it expands creating a global metallic phase. This evolution characteristic could be tied to our most striking observed difference, which is the stripe phase in the Ti doped sample being in a different electronic state compared to the two terminal phases. While no such evidence could be found for the Mn-doped counterpart.

CONCLUSION

We report the real space mapping of conductivity during the PM-M to AFM-I in Ti and Mn doped bilayer calcium ruthenate. We observed the emergence of a striped metallic phase competing with the majority phases in a narrow region of the phase transition. We observed differing characteristics in Mn and Ti doped samples and our observations consistent with Transport and magnetization measurements. Both samples have quite a few differing characteristics for the transition, and we have outlined the observations with possible explanations. The study of the MIT physics in such single crystal ruthenate structures can only be performed by a few select noninvasive techniques. Microwave Impedance Microscopy imaging may emerge as a powerful tool to probe the intimate coupling of electronic and lattice order in these strongly correlated systems.

CHAPTER 6 SUMMARY AND OUTLOOK

In this dissertation, we have discussed the working principle of Microwave Impedance microscopy and discussed all the technical details to construct a homebuilt MIM setup. I have outlined the steps required to simulate MIM signals and understand MIM data. Tuning-fork based AFM has been established to be a great substitute for conventional cantilever probes based on optical feedback. The self-sensing capability makes it ideal for a cryogenic setup with limited probe and sample space for an optical feedback setup. A complete description of the working principle for making Tuning-fork based probes with different etched tips was provided. Pulse-tube cryocoolers provide an alternative way to explore low temperature physics [130]. These coolers do not need a supply of wet cryogens and hence can be used indefinitely which is ideal for experiments exploring phase separation in which careful measurements with different levels of stimuli are undertaken which can be a time-consuming process.

I have briefly reviewed the history of Mott insulators. We covered the concepts of band theory and its shortcomings. With the discovery of an insulating state in Transition Metal oxides specifically NiO and the subsequent explanation by Mott and Hubbard, these insulating states receive quite a lot of interest from the scientific community. With various routes to exploration based on building nano-engineering structures, external stimuli (Pressure, strain) tuning of a Mott insulating state, significant progress has been achieved and links to different Strongly correlated phenomena such as unconventional superconductivity, colossal magnetoresistance, quantum criticality, charge/orbital ordering, etc [26] have been observed. Phase coexistence can occur in systems with multiple competing electronic phases, especially in the case of a first order Metal to Insulator transition. A scanning probe technique based on visualizing and differentiating regions based on local conductivity will allow to extract key insights about the underlying mechanisms and the factors affecting the transition. In this regard, several scanning probe techniques such as Conductive Atomic Force Microscopy (C-AFM), Scanning Near-Field Optical Microscopy (SNOM) and Scanning Tunneling Microscopy (STM) have been utilized.

In this field, Microwave Impedance Microscopy has been established itself as a tool which was able to directly observe the phase separation when a system undergoes a phase transition from a Mott insulating to a Metallic state. The tip acts like an antenna which is a near field emitter and receiver for microwaves. MIM requires minimal sample preparation compared to other techniques. With the lack of necessity for an external ground electrode, it has significant advantages over STM and C-AFM when it comes to explore Mott Insulating states in bulk crystals. MIM's potential was realized in prior work which demonstrated the ability to image electronic inhomogeneity in CMR manganites and motivated exploration in other TMOs [87,115,129].

Emergent electronic and magnetic state has been reported in the bilayer ruthenate $Ca_3Ru_2O_7$. Upon doping with a small concentration of 3d metals on the Ru sites can change the quasi-two-dimensional metallic state of $Ca_3Ru_2O_7$ into a Mott insulating state with a G-type antiferromagnetic order. We reported through nanoscale imaging, the comparison of Metal-Insulator phase transition in Mn and Ti doped $Ca_3Ru_2O_7$. The energetically competing phases in Ti – doped single crystals during the phase transition highlight a new stripe phase different from the two terminal phases.

Although, stripe-like metallic features are present in Mn doped samples, their orientation and general electronic character is different from the Ti doped counterparts.

Our work highlights the striking differences between the two dopants in the characteristics of the induced phase transition from the parent compound. Concurrent to our research, SNOM based investigations on Ca₂RuO₄ [124] and Ti doped Ca₃Ru₂O₇ [131] have observed different behavior for the phase coexistence and lack of evidence to distinguish the stripe phase from the terminal Paramagnetic Metallic Phase (PMM). Considering all these investigations, there are still quite a few unanswered questions on the nature of the phase transition. At the time of writing of this dissertation we have outlined a plan for years to come to investigate these systems with different levels of doping, twinning, and the nature of dopants. We hope to gather enough experimental evidence to support the formulation of a theory explaining the newly discovered stripe phases. Overall, MIM has yet again proven itself as a valuable tool to investigate Strongly Correlated Physics in Transition Metal Oxides.

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