REAL SPACE AND MOMENTUM SPACE X-RAY SPECTROSCOPY OF PHASE SEPARATED MANGANITES

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Abstract

Mixed-valence manganites have been the subject of intense study since the discovery of colossal magnetoresistance (CMR), whereby an applied magnetic field of a few tesla leads to a decrease in resistivity that varies from about a factor of two to 10 orders of magnitude, depending on the exact composition of the material. That a magnetic field would reduce resistivity was not itself surprising, as it was well-known that metallic manganites are also ferromagnetic. This link could not explain the magnitude of the effect, though. Soon thereafter, manganites were shown to exhibit phase separation, where incompatible phases coexisted. Since its discovery, phase separation has been strongly linked to CMR, although the exact mechanism is not clear. Also a mystery is the reason that phase separation happens in the first place: it happens over a large range of compositions, so it cannot be the result of a the free energy being perfectly balanced between the competing phases.

In this dissertation, I discuss work on La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ (LPCMO), which is the ideal material for studying phase separation in manganites. At low temperatures, it is a ferromagnetic metal, and at the Curie temperature it becomes charge and orbitally ordered, antiferromagnetic, and insulating. The phase transition between the two is first order, with a thermal hysteresis of $>30$ K. I performed resonant elastic soft x-ray scattering measurements, which are sensitive to orbital order and antiferromagnetism, on LPCMO to study the temperature dependence of those phases. To study the ferromagnetic metallic phase, I took images using a x-ray photoemission electron microscope (PEEM), which measures x-ray absorption spectroscopy at high spatial resolution. The two datasets show strong evidence for glassy behavior over most of the temperature range where there is electronic order. A glass is a system
that does not reach its equilibrium state in an “experimental” timescale, so this leads to the conclusion that a state with phase separation is not the ground state. Below the Curie temperature, the magnetization has an unconventional temperature dependence, which is consistent with a battle between the two types of order over control of the boundaries between them.

The band structure of mixed-valence manganites contains important information, so there have been a series of angle-resolved photoemission measurements on bilayered $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$. This is the only manganite system that is currently possible to measure using that technique, as it can be cleaved in vacuum to create a surface that has never been exposed to air and has a high enough conductivity to avoid space charge. Unfortunately, different studies have produced conflicting data. One theory is that the samples contain “stacking faults,” which are inclusions of $n$-layered manganites, $n > 2$. The PEEM is sensitive to chemical inhomogeneities, so I used it to image $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. My results confirmed that there are indeed stacking faults, and that they are responsible for the magnetic anomalies that had been observed in bi-layered systems above the nominal Curie temperature.

This dissertation is organized as follows. In chapter 1, I introduce manganites, including the two systems that I measured; soft x-rays; and the two techniques that I used. Chapter 2 is about my measurements of $\text{La}_{0.35}\text{Pr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3$, and chapter 3 about those on $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. Finally, I discuss the current state of research on mixed-valence manganites, including some open questions and some possible future experiments, in chapter 4.
Acknowledgements

Science is at its nature a collaborative activity, and I would like to thank those who collaborated with me to produce the results contained in this dissertation. My research adviser, Jo Stöhr, gave me a great deal of independence throughout my research, so much so that it was a little disorienting at first. While it meant that I did not take the most direct path to the PhD, it created opportunities for my personal growth that may not have been there otherwise. Jo also always made sure I was asking the important questions. Why are the measurements I want to do important? Has my data analysis fully uncovered the implications of my results? Shampa Sarkar and I began the manganite project, and she was always a voice of encouragement when things were not working, helping to keep me motivated to push forward.

I took all of the measurements in this dissertation with Suman Hossain, who joined the manganite project right around the time that things were finally starting to work. I did not know that it was possible to be as enthusiastic about measurements on the fifth day of beamtime as on the first, but Suman was, and it helped me to keep focused on my measurements. He also helped me to be aggressive in getting feedback about my measurements, both early on, when we were still attempting to formulate a model and looking for ideas, and later, when we had that model and were looking for feedback and refinements. It has been a privilege to work so closely with him.

I performed all of my measurements at user facilities, and I need to thank the people who built and maintained the experimental systems that I used. I took some of the resonant elastic soft x-ray scattering (RSXS) data at the Advanced Light Source at Lawrence Berkeley National Laboratory using Yi-De Chuang’s scattering chamber. I would also like to thank Yi-De for all of the discussions we had, both about
the technical details of how best to perform my experiments and about the analysis of the data. Alejandro Cruz and Nadeem Tahir also assisted with his scattering chamber. I also had the opportunity to perform RSXS measurements at the Canadian Light Source, with the assistance of Feizhou He, Andrew Achkar, Ronny Sutarto, and David Hawthorn. I also took photoemission electron microscopy images using PEEM3 at the Advanced Light Source. I was one of the first users to take data below room temperature, and I would like to thank Andreas Scholl and Andrew Doran for their hard work both getting the microscope working and making continuous improvements, especially in the cooling performance. Andreas, Andrew, and Tony Young also provided excellent user support, allowing me to most efficiently use my time at PEEM3.

I would also like to thank the other members of the Stöhr group for everything over the years. Many made direct contributions to my research, and it was truly a pleasure to work with everybody in the group. The administrative staffs at the Applied Physics Department, at SSRL, and at SIMES made everything run smoothly so that I could concentrate on doing science.

The friends I made over the last \(7\frac{1}{2}\) years made graduate school a really enjoyable experience, even when things were not going well with my research. I was also able to get back into athletics as a member of the Stanford Triathlon Team. I did not realize how much I missed organized swim workouts until I got back into the habit, and the Bay Area is a wonderful place to explore on a bicycle or in running shoes, especially with a great group of people.

Finally, I would like to thank my family for everything over the years. My brother David has always been a source of encouragement and made the wise decision to move to the Bay Area for graduate school. For my whole life, my parents have offered their unconditional support for whatever path I wanted to follow, and their faith in me and love for me has meant the world.
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Chapter 1

Introduction

Manganites have been the subject of intense study since the discovery of colossal magnetoresistance (CMR), whereby the application of a magnetic field of a few tesla causes an increase in conductivity of up to a few orders of magnitude [1, 2, 3, 4, 5]. This effect is in part the result of phase separation: there are many types of electronic order that can occur in manganites, including ferromagnetism, antiferromagnetism, charge order, and orbital order. While one phase usually dominates, multiple incompatible phases (e.g. ferromagnetism and antiferromagnetism) can be present within the same crystal at the same time, but spatially separated [6]. Soft x-rays are an ideal tool for measuring each phase individually, and two techniques, photoemission electron microscopy and resonant elastic soft x-ray scattering, combine to provide information about the types of order present, and domain size.

1.1 A Brief Overview of Manganites

1.1.1 Atomic and Electronic Structure

The building block for all manganites is the perovskite unit cell, illustrated in the left column of figure 1.1. The atoms at the corners, labeled “A” in the figure, do not participate directly in the system’s magnetism or electrical conduction, so discussions of electronic properties concern only the MnO$_6$ octahedra. The simplest manganites
are infinite repetitions of this unit cell and have the chemical formula AMnO$_3$, where A is a combination of rare earths and alkali earths. Ruddlesden and Popper showed that layered perovskites, with additional AO layers every $n$ perovskite unit cells, can be grown \cite{7, 8}. Such manganites have a chemical formula of $A_{n+1}Mn_nO_{3n+1}$, and generally are grown such that $n = 1$ or 2. These crystal structures are illustrated in figure 1.1 The layered structures cleave easily, so they are favored for surface-sensitive experiments such as angle-resolved photoemission spectroscopy, which require the sample to be cleaved in vacuum. This dissertation focuses on work done on two different manganite compounds: perovskite $La_{0.35}Pr_{0.275}Ca_{0.375}MnO_3$, and bi-layered $La_{1.2}Sr_{1.8}Mn_2O_7$.

While the atoms on the A sites do not participate in any of the interactions that make the manganites so interesting, they play a critical role in determining the material’s electronic properties. The simplest effect they have is determining the filling of the conduction band. Rare earths lanthanum and praseodymium have a valence of +3 in manganite systems, whereas alkaline earths, such as calcium and strontium, have a valence of +2. Mixing atoms from these two groups results in a mix of $Mn^{4+}$ and $Mn^{3+}$ in the manganese sublattice.

For both valences of manganese, the only partially full electron shell is the 3d shell. Figure 1.2 shows the configurations for the +3 and +4 valence atoms. There is an energy splitting between the localized $t_{2g}$ and itinerant $e_g$ states due to the crystal field \cite{6}. The exchange coupling is larger than the $t_{2g}$-$e_g$ splitting, so all of the electrons on a given manganese atom have the same spin, and the coulomb interaction dictates that the $Mn^{2+}$ state is energetically unfavorable.

Early interest in manganites was generated by the discovery that changing the $Mn^{3+}/Mn^{4+}$ ratio can have a profound effect on the interactions of neighboring manganese atoms in manganites. The first comprehensive experimental study of was Wollan and Koehler’s 1955 neutron diffraction study that mapped out the ground states of manganites in the $La_{1-x}Ca_xMnO_3$ series \cite{9}. In the accompanying theoretical work, Goodenough explained why some neareast-neighbor interactions in $La_{1-x}Ca_xMnO_3$ are ferromagnetic while others are antiferromagnetic \cite{10}. This work served as the basis for the Goodenough-Kanamori rule, which describes nearest-neighbor magnetic
1.1. A BRIEF OVERVIEW OF Manganites

Figure 1.1: The unit cells for $n = \infty$, $n = 1$, and $n = 2$ members of the Ruddlesdon-Popper series [7, 8]. Mn-O bonds are shown for clarity.
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Figure 1.2: Top: the valence states of the 3d shell, showing the occupation for Mn$^{3+}$ and Mn$^{4+}$ ions. Middle: The $e_g$ electron can be either itinerant, as shown on the left, or localized, as shown on the right. Hopping is allowed only if the neighboring atoms have parallel magnetic moments, while virtual hopping of the $t_{2g}$ electrons can lead to nearest-neighbor antiferromagnetic coupling when the $e_g$ electron is localized. Bottom: the ground states that result. The state on the bottom right is known as CE type order, and includes charge order, orbital order, and antiferromagnetism.
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interactions in solids in more general terms [11, 12].

Two of the ground states that Wollan and Koehler discovered are the most-studied states in mixed valence manganites, and all of the work in this dissertation was on systems with those ground states, which are illustrated at the bottom of figure 1.2. The first is the ferromagnetic metallic state, where the \( e_g \) electrons are itinerant. An \( e_g \) electron most easily hops from one site to the next if the \( t_{2g} \) electrons on the two sites have parallel spins, as illustrated in the middle of figure 1.2, so metallic behavior in manganites is always accompanied by ferromagnetism\(^1\). The other prevalent state is insulating, and includes multiple types of electronic order. It is illustrated in the lower right corner of figure 1.2, and the types of order present are as follows: the \( e_g \) electrons are localized, resulting in a checkerboard pattern of Mn\(^{3+}\) and Mn\(^{4+}\). This is charge order. Localized \( e_g \) electrons present an opportunity for Jahn-Teller distortions, which are illustrated in figure 1.3. Because they also affect neighboring sites, Jahn-Teller distortions are most efficient when they occur collectively. The result of this is orbital order: the \( e_g \) electrons sit in the \( d_{3x^2-r^2} \) and \( d_{3y^2-r^2} \) orbitals, forming what appears to be a staircase. Charge and orbital order appear simultaneously due to the coupling provided by the Jahn-Teller distortions, at a temperature denoted \( T_{CO/OO} \), or sometimes \( T_{CO} \) or \( T_{OO} \). There can also be spin order, where spins within a staircase couple ferromagnetically, while they are coupled antiferromagnetically between staircases. The total magnetization is zero, so this phase is antiferromagnetic. Wollan and Koehler categorized a few types of antiferromagnetic order, and their designation of this staircase order CE type has become the standard name for it [9]. The antiferromagnetism is not required for charge and orbital order, so the Néel temperature \( T_N \leq T_{CO/OO} \), with equality holding only in a few special cases.

\( ^1 \)There is an antiferromagnetic metallic state in La\(_{1-x}\)Sr\(_x\)MnO\(_3\), but it is still an example of the marriage of ferromagnetism and metallicity: The antiferromagnetism is A-type, which means that there are alternating planes of spin up and spin down, so each manganese atom has four nearest neighbors that are ferromagnetically coupled and only two that are antiferromagnetically coupled. The system displays metallic behavior only parallel to the ferromagnetically coupled planes; transport measurements conducted perpendicular to those planes reveal insulating behavior. Near half doping, the high temperature phase is paramagnetic metallic rather than insulating, but this phase has not been extensively studied.
Figure 1.3: Jahn-Teller distortions, which are the result of an unpaired, localized $e_g$ electron. The introduction of a lattice distortion lowers the energy level of the $e_g$ electron. Jahn-Teller distortions are favorable when the energy cost of the lattice distortion is less than the energy gained by lowering the electron energy level. (from [13])
1.1. A BRIEF OVERVIEW OF MANGANITES

The ferromagnetic metallic and charge/orbital/antiferromagnetically ordered insulating phases are very different, and the fact that both occur in manganites shows how close in energy they are. Critical in determining which phase dominates is the size of the hopping interaction $t$ in comparison to those which tend to localize the $e_g$ electrons, such as the antiferromagnetic $J_{AF}$ which arises from virtual hopping between $t_{2g}$ electrons, the coulomb interaction, and the collective Jahn-Teller distortions. [6, 14]. In cases where $t$ is large, also referred to high-bandwidth cases because a large hopping interaction results in a wide valence band, the ferromagnetic metallic phase is the ground state, whereas low-bandwidth manganites are insulating.

There are two factors that determine which interactions dominate in a particular manganite: doping (the Mn$^{3+}$/Mn$^{4+}$ ratio) and the size of the A-site ions. In La$_{1-x}$Ca$_x$MnO$_3$, as is standard for manganites, $x$ represents the fraction of manganese atoms that are Mn$^{4+}$, so $1 - x$ are Mn$^{3+}$. In Wollan and Koehler’s study, of La$_{1-x}$Ca$_x$MnO$_3$, they found that the ferromagnetic metallic phase exists for $0.17 < x \leq 0.5$, and the purely charge, orbital, and antiferromagnetic phase from $0.5 \leq x < 0.875$ (at $x = 0.5$, the ferromagnetic metallic phase exists at intermediate temperatures, and there is charge and orbital order and antiferromagnetism at low temperatures) [9]. In general, the ferromagnetic metallic phase exists only in the $x \leq 0.5$ range, where there are more Mn$^{3+}$ than Mn$^{4+}$. The collective Jahn-Teller distortions of charge and orbital order become less energetically favorable in this case because the sites labeled Mn$^{4+}$ in the lower right corner of figure 1.2 now contain extra charge$^2$, which means that the collective lattice distortions raise the energy of an $e_g$ electron that is not there for the $x \geq 0.5$ case. The ferromagnetic metallic phase also requires there to be a mix of Mn$^{3+}$ and Mn$^{4+}$ in the system, because there need to be $e_g$ electrons to hop and empty $e_g$ orbitals for them to hop to, so it does not appear for $x$ close to 0 or 1.

Substituting one A-site atom for another with the same valence, such as praseodymium for lanthanum, also shifts the balance between ferromagnetism and charge/orbital order [14]. The size of the A-site ions affects the lattice structure, as the manganese

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$^2$Referring to them as Mn$^{3+}$ and Mn$^{4+}$ is an oversimplification; the same is true for saying that all of the oxygens are O$^{2-}$. While the manganese atoms do have different valences, they are all closer to 3.5+. 
and oxygen atoms need to move to accommodate larger or smaller atoms. The effect on the lattice is best described by the angle of Mn-O-Mn bonds. In the ideal cubic structure, that angle is 180°. In manganites, the manganese octahedra are tilted, so the angle is less than 180°. Conduction occurs as a result of hybridization between the manganese 3d and oxygen 2p electrons. The 2p orbitals have lobes along the cartesian coordinate axes, so as the Mn-O-Mn bond angle deviates more and more from 180°, the degree of hybridization decreases. This leads to a decrease of t and thus charge/orbital order, with localized eg electrons, becomes favored over a ferromagnetic metal. We see this in Pr_{1-x}Ca_xMnO_3, which never exhibits the ferromagnetic metallic phase. As an example, Pr_{0.6}Ca_{0.4}MnO_3, illustrated in figure 1.4, has Mn-O-Mn bond angles of about 155°.

As in all solids, charge carriers in manganites are not free electrons or holes, but quasiparticles. In manganites, those quasiparticles are polarons, which are coupled electrons and lattice distortions. This designation is most obvious in the case of charge and orbital order, where there are Jahn-Teller distortions on the Mn^{3+} sites. In the ferromagnetic metallic phase, the polarons are delocalized, so the lattice distortions are spread evenly among many lattice sites. The difference between this and an
undistorted lattice is a matter of semantics: we could say that each unit cell exhibits the same distortion from the unit cell that would theoretically exist if there were no polarons (a system of all Mn$^{4+}$), or that there are no lattice distortions because the structure is uniform. I will generally refer to the ferromagnetic metallic phase as undistorted to distinguish its structure from the collective lattice distortions in the charge and orbitally ordered phase. In the paramagnetic insulating phase, there are no long-range collective lattice distortions, but there have been observations of single polarons [16].

The two materials discussed in this dissertation have $x$ of 0.375 and 0.4, but very different electronic phase diagrams. La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ is a ferromagnetic metal below $T_C \approx 120$ K (its infinite-layer counterpart La$_{0.6}$Sr$_{0.4}$MnO$_3$ has $T_C \approx 370$ K). La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ exhibits both ground states. Below $T_C \approx 80$ K cooling and 120 K warming, it is a ferromagnetic metal. Between $T_C$ and $T_{CO/OO} \approx 210$ K, it is charge/orbitally ordered, and antiferromagnetic.

1.1.2 Colossal Magnetoresistance and Phase Separation

Colossal magnetoresistance (CMR) was first measured by Kusters et al. in 1989, who showed that a field of 11 T caused a reduction of resistivity of about two orders of magnitude in single-crystal Nd$_{0.5}$Pb$_{0.5}$MnO$_3$ [1]. Partially because the authors did not realize the importance of their measurements, that work received little attention and it would be a few years before the phenomenon led to the blossoming of the field. In 1993, Chahara et al. measured a 53% reduction in resistivity of a La$_{0.72}$Ca$_{0.25}$MnO$_x$ thin film when they applied a magnetic field of 1 T at 220 K [2], and von Helmolt et al. measured a 60% reduction in resistivity of a La$_{2/3}$Ba$_{1/3}$MnO$_x$ thin film in an applied magnetic field of 6 T at room temperature [3]. In 1994, Jin et al. discovered that applying a magnetic field of 6 T to a La$_{0.67}$Ca$_{0.33}$MnO$_x$ thin film at 77 K caused the film’s resistivity to decrease by a factor of 1270$^4$. Also of interest is that the direction

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$^3$In all of the thin film experiments mentioned in this paragraph $x \approx 3$, but getting oxygen stoichiometry correct in thin films is tricky, and the problem had not been solved when these experiments were performed.

$^4$The authors thus set the convention for reporting CMR as $(R_{H=0} - R_H)/R_H$, which produces larger numbers than other possible expressions but is necessary when the effect on resistivity is so
of the applied field did not have any bearing on the magnitude of the CMR. All of these compounds have a ferromagnetic metallic ground state, and in the absence of a magnetic field, conductivity is high within individual ferromagnetic domains, but interdomain conductivity is low because the magnetic moments of the 3$d$ electrons are not aligned from domain to domain. Early speculation was that the applied magnetic field served to align the magnetic domains in the direction of the field, whatever it was, eliminating the domain walls that decreased the bulk conductivity. In 1995, A. J. Millis et al. showed that this picture was incomplete, and that the true mechanism of CMR must be more complicated [17].

Soon thereafter, the notion that multiple phases coexist came up [18], and in 1999 Fäth et al. showed that the metal-insulator transition was spatially inhomogeneous in La$_{0.7}$Ca$_{0.3}$MnO$_3$ [19], while Uehara et al. showed that the charge/orbital order phase does not cover the whole sample in La$_{0.675-y}$Pr$_y$Ca$_{0.375}$MnO$_3$, even when it is the only ordered phase present [20]. The exact nature of the phases that coexist with the dominant phases is still not completely clear, as they are harder to measure in isolation. Phase separation is thought to play a key part in CMR, so identifying all phases and explaining their interactions is critical [21].

I chose La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ (LPCMO) for these measurements because it straddles the boundary between being a ferromagnetic metal and a charge/orbital ordered, antiferromagnetic insulator. This is shown in the phase diagram in figure 1.5. The parent compounds are La$_{0.625}$Ca$_{0.375}$MnO$_3$, which has a ferromagnetic metallic ground state, and Pr$_{0.625}$Ca$_{0.375}$MnO$_3$, which is never metallic and has a ground state of charge and orbital order and antiferromagnetism. Both compounds have the same doping $x = 0.375$, so the only thing that changes as one moves across the phase diagram is the tilting of the MnO$_6$ octahedra, as Pr$^{2+}$ has a smaller radius than La$^{2+}$. For intermediate values of $y$, ferromagnetism exists but is suppressed relative to $y = 0$, with $T_C$ falling as the praseodymium $y$ is increased. When $T_C$ falls below 210 K, charge/orbital order sets in at that temperature [20]. The smooth shift from one phase to another as a function of $y$ makes LPCMO the ideal material for measuring phase separation, as there should be plenty of evidence of the competition between the two dramatic, much as $\gamma$ is a more useful number than $v/c$ when talking about relativistic particles.
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Figure 1.5: The $\text{La}_{0.625-y}\text{Pr}_y\text{Ca}_{0.375}\text{MnO}_3$ phase diagram. $\text{La}_{0.35}\text{Pr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3$, discussed in this dissertation, is indicated with a dashed line. The phase transition between the ferromagnetic metallic and charge/orbital ordered insulating phase has a thermal hysteresis for most of the compounds where it occurs; this is indicated by two dashed lines.
phases. I will discuss this competition in depth in chapter 2.

Another area of interest in the manganites is the band structure: with coexisting metallic and insulating phases, it is natural to wonder what the bands look like around the fermi surface. As I will discuss in chapter 3, the answer has not been straightforward, as measurements of the band structure of La$_2$Sr$_x$Mn$_2$O$_7$ have produced conflicting results, with some but not all experiments showing evidence of quasiparticles at the fermi energy. I will discuss measurements that explain why there are inconsistencies between the various measurements.

1.2 X-Ray Techniques

Bright, polarized, monochromatic x-rays produced at synchrotron radiation facilities have made possible many experiments in scientific disciplines ranging from biology to geology to materials science, including all of the work discussed in this dissertation [22]. I performed photoemission electron microscopy (PEEM) measurements at the PEEM3 endstation at the Advanced Light Source (ALS) in Berkeley, California, and resonant elastic soft x-ray scattering (RSXS) measurements at the ALS and at the Canadian Light Source (CLS) in Saskatoon, Saskatchewan. Below I will discuss some of the basics of soft x-rays, which are those x-rays with photon energy below 2000 eV, and the two techniques that I used.

1.2.1 Soft X-Ray Absorption Spectroscopy

Soft x-rays are an ideal tool for measuring 3$d$ metal oxides for a number of reasons. X-rays provide elemental specificity, achieved by tuning the photon energy to a resonance, or edge. For all of the 3$d$ metals, the $2p \rightarrow 3d$ transition, referred to the $L_{2,3}$ edge, occurs in the soft x-ray regime. For manganese, the $L_3$ edge ($2p_{3/2} \rightarrow 3d$) is about 640 eV and the $L_2$ edge ($2p_{1/2} \rightarrow 3d$) is about 650 eV. Meanwhile, the oxygen $K$ edge ($1s \rightarrow 2p$) is at 520 eV, so the same experimental setup can probe properties of both the manganese and oxygen atoms separately. Figure 1.6 shows an x-ray
Figure 1.6: An absorption spectrum of $\text{La}_{0.35}\text{Pr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3$, taken at 190 K with linear horizontal polarized x-rays, showing both the oxygen and manganese edges. Also labeled are the manganese $L_3$ and $L_2$ peaks and the oxygen edge jump, which is the result of photons being able to excite 1s oxygen electrons into the continuum of unoccupied states above the Fermi energy.

absorption measurement that includes both the oxygen and manganese edges. Generally, we measure much narrower ranges, focusing on one element or even one energy at a time.

Because they directly probe the valence band, soft x-rays can provide a wealth of useful information. In compounds, the shape of the absorption edge varies as the atomic valence varies, for example, from $\text{Mn}^{2+}$ to $\text{Mn}^{3+}$ to $\text{Mn}^{4+}$ [23]. Even at the oxygen edge, there is plenty of useful information. Neighboring oxygen and manganese orbitals hybridize, so a change in the shape of the oxygen peak at the onset of the edge can indicate a metal-insulator transition [24].

X-ray absorption is also an extremely useful tool for studying magnetism. The x-ray absorption of ferromagnetic materials depends on the polarization of the incoming x-rays, in an effect known as x-ray magnetic circular dichroism (XMCD). Figure 1.7a shows spectra of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ taken with opposite circular polarizations, and their difference, which is the XMCD signal, is shown in figure 1.7b. Spectroscopy measures
Figure 1.7: (a) X-ray absorption spectra taken on Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ in a 2 T field at 25 K with left and right-hand circularly polarized photons. (b) The x-ray magnetic circular dichroism (XMCD), which is the difference of the two spectra in (a), as a function of photon energy.

the average properties of the sample, so the spectra were taken in a 2 T field to align the magnetic moments. At a given energy, the XMCD signal is proportional to $\mathbf{L}_{\text{photon}} \cdot \mathbf{M}_{\text{Mn}}$, where $\mathbf{L}_{\text{photon}}$ is the angular momentum of the circularly polarized photon, which in parallel to the photon wavevector $\mathbf{k}$ for right-handed circularly polarized light and antiparallel to $\mathbf{k}$ for left-handed circular polarization, and $\mathbf{M}_{\text{Mn}}$ is the magnetization of the manganese atoms. XMCD can thus be measured either by changing polarization of the incoming photons, as we did, or by changing the direction of the applied field to change the magnetization.

1.2.2 Photoemission Electron Microscopy

We took x-ray images of manganites using photoemission electron microscopy (PEEM). A simple schematic of PEEM is illustrated in figure 1.8a. The rate of photoemission...
is directly proportional to the x-ray absorption, so PEEM allows us to do x-ray absorption with high spatial resolution. In particular, we can take a series of images at different x-ray energies and compare the absorption spectrum of specific regions within the images. I will discuss this type of measurements in Chapter 3. We also used the PEEM to directly image ferromagnetic domains via XMCD. Unlike bulk XMCD measurements, this does not require applying a magnetic field, as we can resolve individual ferromagnetic domains. This is especially important in manganites, where magnetic fields can cause phase transitions. Figure 1.8b illustrates the standard scheme for generating images with only magnetic information.

As illustrated in figure 1.7b, the maximum XMCD occurs at the absorption peak at the $L_3$ edge. Because we were interested in imaging magnetic domains rather than looking at the spectral features of the dichroism, we sat at that energy and took many images, alternating x-ray polarizations. There are two non-ferromagnetic phases present in La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$: the disordered paramagnetic insulating phase and the charge/orbital/antiferromagnetic ordered phase. We put considerable effort into distinguishing the two, as doing so would have allowed us to show how the three phases coexist spatially. The charge/orbital/antiferromagnetically ordered phase in manganites has been imaged using electron microscopy [20, 25, 26, 27], but that technique is not capable of distinguishing ferromagnetic regions from paramagnetic regions, so there were not yet images that distinguished between all three phases. To distinguish between the two non-ferromagnetic phases, we would need a contrast mechanism: we were looking for a difference in the x-ray absorption spectra of the two phases. We did not see any signs of contrast that might allow us to distinguish between these two phases, so we were not able to produce images with all three phases labeled. There are no bulk x-ray absorption measurements that show spectral changes between the paramagnetic insulating phase and the charge/orbital/antiferromagnetic ordered phase, so any contrast mechanism between them would be weak, and we

---

5Switching polarizations requires changes at the source of the x-rays, so the beams with $\sigma^-$ and $\sigma^+$ polarization do not overlap exactly. This is important with a full-field imaging technique such as PEEM, as it adds significant artifacts to our XMCD images. To compensate for this difference, we took many images at temperatures where there were no ferromagnetic domains and averaged the XMCD for all of them, giving us a background image. We then subtracted that background image from each of the individual XMCD images.
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Figure 1.8: (a) The PEEM setup. X-rays come in at an angle to the sample surface (30° at PEEM3), and the photoelectrons are focused onto a phosphor, which is imaged by a CCD. (b) The scheme for obtaining magnetic images from PEEM images. We took raw images with left circular (σ−) and right circular (σ+) x-rays at the manganese L₃ edge. No sample surface is uniform, so these images include topographic as well as magnetic information. By taking the pixel-by-pixel asymmetry (sum divided by difference) of images with opposite circular polarization, we generate an image that contains only magnetic information. Black and white represent magnetization pointing in the opposite direction.

would require many images to produce data with a sufficient signal-to-noise ratio. Doing so for all possible energies around the manganese and oxygen absorption edges would require much more beamtime than is available.

The PEEM3 is unique in that it has cooling capabilities. We performed some of the first measurements below room temperature on the microscope, and over the course of my time as a student, the PEEM3 staff improved the performance of the cooling system. As a result, the minimum temperature achievable at the PEEM3 was not the same for all of my measurements.

1.2.3 Resonant Soft X-Ray Scattering

We measured the charge/orbital/antiferromagnetic ordered regions using resonant soft x-ray scattering (RSXS). X-ray scattering is an excellent tool for measuring periodic structures, which include the alternating magnetic moments in antiferromagnetism and the ordered pattern of eg electrons in orbitally ordered manganites. Before I get into the specifics of RSXS, I will introduce the concept of x-ray diffraction, which
1.2. X-RAY TECHNIQUES

1.2.1. X-RAY TECHNIQUES

Figure 1.9: The principle of x-ray diffraction, illustrating Bragg’s Law.

is mainly used to measure atomic positions in crystalline materials.

Figure 1.9 illustrates the basics of x-ray diffraction. Incoming photons diffract off of atoms in the crystal, and photons that diffract off of different atoms interfere with each other. If the light diffracted off of each atom is in phase with photons diffracted off of other atoms, there is constructive interference and a measurable diffraction signal. To simplify the discussion, we will group the atoms into planes and specify that the incoming and outgoing photons’ wavevectors each make the same angle $\theta$ to these planes. The incoming and outgoing wavevectors, $k_0$ and $k_f$ respectively, are shown meeting this condition in figure 1.9. This ensures that photons scattering off of atoms within the same plane interfere constructively, much as the angle of incidence equals the angle of reflection for a mirror.

For interplane interference, we look at the path length difference of photons scattering off of atoms in neighboring planes. If the path length difference is a whole number of wavelengths, the diffracted photons are in phase, and they interfere constructively. As illustrated in the bottom two planes in figure 1.9, the path length difference of the incoming leg is $d \sin \theta$, where $d$ is the spacing between diffraction

$q = k_f - k_0$

\[ q = k_f - k_0 \]

\[ k_0 \quad \theta \quad d \sin \theta \]

\[ k_0 \quad \theta \quad d \sin \theta \]
planes. The outgoing leg is the same, so we arrive at a total path length difference of $2d \sin \theta$, resulting the Bragg condition

$$n\lambda = 2d \sin \theta$$

where $n$ is an integer. Note that for $\lambda > 2d$, diffraction is impossible, as the experiment would require that $\sin \theta > 1$. If this is the case, we say that the diffraction limit prevents us from making the measurement. Practically, the diffraction limit for a given $d$ occurs at a slightly shorter wavelength, as reaching the diffraction limit exactly would require the detector to be in the path of the incoming x-rays.

Because wavelength is not standard from experiment to experiment, a more useful quantity in diffraction is the momentum transfer $q = k_f - k_0$, which is illustrated in figure 1.9. Noting that $k = 2\pi/\lambda$, we can see that $k_f \cdot q = -k_0 \cdot q = (2\pi/\lambda) \sin \theta$, so $q = 2(2\pi/\lambda) \sin \theta$. Thus we can rewrite the Bragg condition as

$$q \cdot d = 2\pi n$$

This is just another way of stating that the x-rays diffracted from successive planes have a phase difference of $q \cdot d$, and there is a diffraction signal when that phase difference is a multiple of $2\pi$.

X-ray diffraction is generally used to determine crystal structures. These experiments are performed with hard x-rays, which have the short wavelengths required to reach the necessary values of $q$, and the ability to penetrate deeply into the crystal. They are sensitive mainly to atomic positions within the crystal.

To measure electronic order, we need to exploit resonant enhancements that occur when the photon energy is carefully chosen. The scattering factor $f$ is generally expressed as

$$f = f_0 + f'(E) + if''(E)$$

where $f_0$, $f'$, and $f''$ are all real. $f_0$ is the non-resonant Thomson term, which only weakly depends on energy, and $f'$ and $f''$ are the resonant terms, which are sensitive to electronic order. Hard x-ray diffraction is generally not performed at resonant
photon energies, so \( f_0 \) is the only term that contributes to the diffraction signal. In RSXS, on the other hand, the resonant terms are responsible for the measured signal. \( f'' \) is of particular interest to x-ray spectroscopists because it is the absorption term: the x-ray absorption signal

\[
I_{\text{absorption}} \propto \sum_{\text{unit cell}} f''(E)
\]  

(1.4)

In scattering, we get a phase factor and we measure all components of \( f \), yielding

\[
I_{\text{scattering}} \propto \left| \sum_{\text{unit cell}} e^{i\mathbf{q} \cdot \mathbf{r}} (f_0 + f'(E) + if''(E)) \right|^2
\]  

(1.5)

where \( \mathbf{r} \) is the position of an atom within the unit cell.

For our measurements, we used soft x-rays because they directly probe the 3d band. We measured superlattice order, which is periodic order with a period of multiple lattice constants. Figure 1.10 shows CE type order, which is present in \( \text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) and \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \). The lattice constants for the structural unit cell are labeled \( a \) and \( b \) in the figure; the unit cell is orthorhombic due to tilting of the oxygen octahedra, as illustrated in figure 1.4.

To see where our signal comes from, we will for the moment consider only the magnetic order. We choose \( \mathbf{q} \parallel \mathbf{a} \) such that \( \mathbf{q} \cdot \mathbf{a} = \pi \). This corresponds to \( n = 1/2 \) in equation 1.2, so this \( \mathbf{q} \) corresponds to the \( (\frac{1}{2} \ 0 \ 0) \) diffraction peak. This means that we are measuring a “forbidden” peak, which is so-called because it does not appear to satisfy the Bragg condition. I will show that within the magnetic unit cell, there is constructive interference between photons scattered from different planes.

In [28], Hill and McMorrow discuss resonant magnetic x-ray scattering in depth. The scattering cross section is

\[
f^{\text{XRES}} = [(\mathbf{\tilde{e}}' \cdot \mathbf{\hat{e}}) F^{(0)} - i(\mathbf{\tilde{e}}' \times \mathbf{\hat{e}}) \cdot \mathbf{\hat{m}} F^{(1)} + (\mathbf{\tilde{e}}' \cdot \mathbf{\hat{m}})(\mathbf{\hat{e}} \cdot \mathbf{\hat{m}}) F^{(2)}] 
\]  

(1.6)

where \( \mathbf{\tilde{e}}' \) and \( \mathbf{\hat{e}} \) are the polarization of the outgoing and incoming beams, respectively; \( \mathbf{\hat{m}} \) is the magnetic moment of the atom being scattered from; and \( F^{(n)} \) is a sum
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Figure 1.10: CE type superlattice charge, orbital, and antiferromagnetic orders in manganites, illustrating the superlattice unit cell (dotted line). The lattice constants $a$ and $b$ for the structural unit cell are labeled. The antiferromagnetic superlattice peak is $q = (\frac{1}{2}, 0, 0)$, which means that $q \parallel a$ and $q \cdot a = \pi$. At the top of the figure, value of $q \cdot r$ is shown for the scattering planes within the superlattice unit cell.

Of matrix elements, which is a function of photon energy and the specific electronic configuration within the material. Therefore, following equation 1.5, the scattered intensity is

$$I \propto \sum_{\text{unit cell}} |e^{i\mathbf{q}\cdot\mathbf{r}} (\langle \hat{\varepsilon}' \cdot \hat{\varepsilon} \rangle F^{(0)} - i (\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{\mathbf{m}} F^{(1)} + (\hat{\varepsilon}' \cdot \hat{\mathbf{m}})(\hat{\varepsilon} \cdot \hat{\mathbf{m}}) F^{(2)})|^2$$

(1.7)

The first term on the right side does not depend on magnetization, so we can define

$$f^0 = (\hat{\varepsilon}' \cdot \hat{\varepsilon}) F^{(0)}$$

(1.8)

Note that this is not the Thomson scattering term $f_0$, as defined in equation 1.5, but rather a resonant term that contributes only to charge scattering.

Because spin up and spin down are antiparallel, we can simplify things by noting that $(\hat{\varepsilon}' \cdot \hat{\mathbf{m}})(\hat{\varepsilon} \cdot \hat{\mathbf{m}})$ has the same value for spin up ($\hat{\mathbf{m}}_\uparrow$) and spin down ($\hat{\mathbf{m}}_\downarrow = -\hat{\mathbf{m}}_\uparrow$), so the third term on the right side of equation 1.6 does not depend on spin and thus we can define

$$f' = (\hat{\varepsilon}' \cdot \hat{\mathbf{m}}_\uparrow)(\hat{\varepsilon} \cdot \hat{\mathbf{m}}_\uparrow) F^{(2)}$$

(1.9)
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The second term of equation 1.6 depends on the spin, but because $\hat{m}_\downarrow = -\hat{m}_\uparrow$ we can define

$$m(\mathbf{r}) = \begin{cases} 1, \text{ spin up} \\ -1, \text{ spin down} \end{cases} \quad (1.10)$$

and

$$f'' = - (\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{m}_\uparrow F^{(1)} \quad (1.11)$$

so that we can rewrite equation 1.7 as

$$I \propto \sum_{\text{unit cell}} |e^{i \mathbf{q} \cdot \mathbf{r}} (f^0 + im(\mathbf{r}) f'' + f')|^2 \quad (1.12)$$

We can evaluate the sum term by term using figure 1.10. The vertical lines represent diffraction planes, where $\mathbf{q} \cdot \mathbf{r}$ is constant, and the colors of the atoms show the values of $m(\mathbf{r})$. Going left to right and top to bottom, choosing atoms at the bottom and left unit cell borders, we can evaluate the sum term by term for the 8 atoms in the orbital/magnetic unit cell:

\[
I \propto \begin{aligned}
&|1 \left[(f^0 + if'' + f') + (f^0 + if'' + f')\right] \\
&+ i \left[(f^0 - if'' + f') + (f^0 + if'' + f')\right] \\
&- 1 \left[(f^0 - if'' + f') + (f^0 - if'' + f')\right] \\
&- i \left[(f^0 + if'' + f') + (f^0 - if'' + f')\right]|^2 \\
&= 16|f''|^2
\end{aligned}
\]

This calculation highlights the power of RSXS. While $f''$ represents a small contribution to the scattering from a single atom, it is the only term that does not cancel out, so we measure it in isolation. This leads to resonance profiles with significantly more structure than x-ray absorption scans, and there are fewer contributions to consider when attempting to model those resonance profiles.

The orbital order also contributes to the RSXS signal; its superlattice peak is at $q = (0 \frac{1}{2} 0)$. We do not see any contribution of orbital order at $q = (\frac{1}{2} 0 0)$ because the orbital pattern in the plane with $\mathbf{q} \cdot \mathbf{r} = 0$ is the same as in the plane with $\mathbf{q} \cdot \mathbf{r} = \pi$. 

so the terms cancel. Likewise, there is no magnetic signal measured at \( q = (0 \frac{1}{2} 0) \).

Our sample is twinned, so we can measure the \( (\frac{1}{2} 0 0) \) and \( (0 \frac{1}{2} 0) \) reflections with the same experimental geometry, and the peak that we measure includes contributions from both. I will discuss this in more depth in chapter 2.

Figure 1.11 shows the two different types of RSXS scans that we performed. The first is the momentum scan, where we scan the magnitude of \( q \). The result of this scan is a peak centered at the \( q \) that satisfies the Bragg condition. The area under the curve tells us about two quantities: the fraction of the sample that is in the ordered state and the order parameter within that fraction. From these measurements we cannot directly disentangle the two, although we expect the order parameter to be higher at lower temperatures due to decreased thermal fluctuations. The width of the curve is inversely proportional to the correlation length of the superlattice order: when \( q \) deviates from its peak value, the Bragg condition is not quite satisfied, so there is a slight phase shift between photons scattered from successive planes. As the number of scattering planes increases, the effect of this phase mismatch is amplified, resulting in destructive interference at smaller deviations from the peak in \( q \). Momentum scans are also called \( \theta - 2\theta \) scans due to the way they are carried out. The incoming x-rays are fixed in space, so the sample is rotated to an angle of \( \theta \) relative to the incoming light. The detector must then be rotated by \( 2\theta \) from the position where it detects the direct beam. When the sample is rotated to measure different values of \( q \), the detector is rotated twice as much.

The other type of scan that we perform is a fixed-\( q \) scan, also called a resonance profile. In this type of measurement, we stay at the same \( q \) (usually the peak) and vary the energy of the incoming photons. To stay at the same \( q \), the sample and detector must be rotated, as in a momentum scan. These measurements are much more difficult to interpret than momentum scans, but they can provide a great deal more information. We use them mostly to tell whether we are measuring the same type of order at different temperatures.

Unfortunately, that determination is not trivial, especially in manganites. Simulations of RSXS resonance profiles work very well for most transition metal oxides, but manganites have inexplicably proved especially difficult to simulate. On top of this,
resonance profiles showing the same type of order are different in different compounds, as can be seen in the measurements of Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ and Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ in [29]. Calculations at the oxygen edge might be simpler, but it is at a lower energy and thus longer wavelength, and the diffraction limit prevents us from performing RSXS measurements there. Thus the only approach we can take to analyzing resonance profiles is to compare them with previous measurements. Early RSXS experiments on manganites [30] were performed on compounds that had been previously analyzed with neutron scattering [31], so the authors were able to determine which resonance profile represented which order. Despite this imperfect method, there is still information to be gleaned from these measurements, as I will show in chapter 2.

Figure 1.11: (a) The geometry of a momentum ($\theta$-2$\theta$) scan. (b) Measured momentum scan on La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ at 160 K. (c) Schematic for fixed-\(q\) RSXS scans (resonance profiles). (d) Measured resonance profile on La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ at 160 K. The arrow in (b) indicates the \(q\) at which the scan in (d) was measured, and the arrow in (d) indicates the energy at which the scan in (b) was measured.
Chapter 2

Electronic Order in
\textit{La}_{0.35}\textit{Pr}_{0.275}\textit{Ca}_{0.375}\textit{MnO}_3

As I discussed in section 1.1.2, LPCMO is the ideal material for studying phase separation. It has two regimes that exhibit different types of electronic order, separated by a highly first-order phase transition. Below the Curie temperature $T_C$ ($\sim 80$ K cooling and $120$ K warming), LPCMO is a ferromagnetic metal. Between $T_C$ and $T_{CO/OO}$ ($\sim 210$ K), there is charge and orbital order and antiferromagnetism. The exact value of the Néel temperature $T_N$, where the antiferromagnetism sets in, is unclear, although as I will show below, it is probably the same as $T_{CO/OO}$. I used PEEM to image the ferromagnetic domains and RSXS to measure the superlattice orbital and antiferromagnetic order. Figure 2.1 shows data taken above and below $T_C$. Above $T_C$ the PEEM image shows no ferromagnetism while there is a strong RSXS signal. Below $T_C$ there is a nonzero RSXS signal, indicating that superlattice order coexists with the ferromagnetic phase. The RSXS data indicate that the correlation length of the superlattice order is less than 150 nm, while the widths of the domain walls in the PEEM images suggest a magnetic resolution of 200 nm. Thus it is not surprising that the non-ferromagnetic regions are not visible in the PEEM image taken at 60 K. There is also a strong thermal hysteresis in the RSXS data, which I will discuss in depth below.
Figure 2.1: Momentum scans (left) and PEEM images (right) of LPCMO above and below $T_C$. There is a strong thermal hysteresis in the RSXS data, but the PEEM images look the same for both warming and cooling at these temperatures.
Figure 2.2: A schematic of accommodation strain. The white region is the unstrained parent crystal and the dark green region is an intrinsically strained phase. The light green region is not intrinsically strained but exhibits accommodation strain.

2.1 The Role of the Lattice

The ordered phases are incompatible and thus never overlap, so they interact through the lattice. As I mentioned in section 1.1.1, charge and orbital order result in collective lattice distortions, while the ferromagnetic metallic phase thrives in a relatively undistorted lattice. These collective lattice distortions change the crystal structure in the regions where they occur, while the original structure survives outside of the distorted regions. Because the lattice distortions do not introduce structural defects, at the interface between the distorted and undistorted regions there is accommodation strain, which is the long-range relaxation of the lattice distortions, as illustrated in figure 2.2. If the undistorted regions are paramagnetic insulating, as they are above $T_C$ in LPCMO, the only energy cost of accommodation strain is the cost of distorting the lattice from its equilibrium.

Below $T_C$, the ferromagnetic metallic phase and accommodation strain inhibit each other: the regions of accommodation strain deviate more from the ideal cubic perovskite structure than the rest of the crystal, suppressing the hopping interaction. Thus the presence of the ferromagnetic metallic phase raises the energetic cost of accommodation strain, as it interferes with both the lattice and electronic order. A reasonable question to ask, then, would be why the collective lattice distortions exist...
at all below $T_C$ if, by all appearances, they are not energetically favorable. Before I address that question, I will discuss the dynamics above $T_C$, as they have been more thoroughly studied and will be relevant below $T_C$.

The direct paramagnetic insulator to ferromagnetic metal phase transition has long been a subject of study in manganites where it occurs. It has been shown to be first-order in some compounds [32, 16, 33], including bi-layered La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ ($x \approx 0.4$) and La$_{0.7}$Ca$_{0.3}$MnO$_3$. Neutron and x-ray diffraction measurements of these materials showed that there are small regions of collective lattice distortions at the $q$ that is associated with CE type order [32, 16]. The correlation length of these regions was small ($< 1$ nm), which corresponds to about the size of the unit cell of CE type order, as shown in figure 1.2. The key findings of these studies was that the polarons above $T_C$ are glassy. In the broadest sense, a “glass” is a system that does not achieve its ground state in “experimental” timescales, so in this case the meaning of “glassy” is essentially “frozen,” in that the polarons do not fluctuate. The exact mechanism of this freezing is unclear, but the glassy polarons inhibit the formation of the ferromagnetic metallic phase at $T_C$, resulting in a first-order phase transition.

In the materials investigated in these studies, the diffraction signal was extremely weak below $T_C$, so the authors could not make any statements about the superlattice order that coexists with the ferromagnetic metallic phase. Also, neutron and non-resonant hard x-ray diffraction are sensitive only to atomic locations, so these studies measured lattice distortions in terms of atomic positions, but not the electronic order that caused those lattice distortions.

### 2.2 Competing Electronic Order in LPCMO

I will show that in LPCMO, collective lattice distortions associated with the charge and orbital order above $T_C$ freeze, and thus are the same phenomenon as the glassy polarons observed in the earlier experiments [16, 32]. In LPCMO, we see not single polarons but superlattice order, which creates a phase transition that is more clearly first-order and which we can study in more detail.
2.2.1 X-ray measurements

I will begin with a discussion of the PEEM images. A series of images from one cooling/warming cycle are shown in figure 2.3a. There is a thermal hysteresis between \( \sim 71 \text{ K} \) and 125 K. In the images that show ferromagnetic domains, the domain pattern does not change from image to image except for those taken near \( T_C \). Figure 2.3b shows in more detail the formation of the ferromagnetic domains on cooling. Above 71 K, they take the form of mostly alternating stripes rather than the large domains present at lower temperatures. The stripes are a sign that there is something fundamentally different about the energy landscape at this range of temperatures than elsewhere in the ferromagnetic region of the phase diagram. I will later show that lattice strain associated with the charge and orbital order inhibits the formation of ferromagnetism, so it is likely also behind this domain pattern. In addition to the large ferromagnetic regions, there are large gray regions, which are not ferromagnetic. This shows that the phase transition temperature is spatially inhomogeneous. On warming, the transition occurs over a much narrower temperature range, as shown in figure 2.3c. The domain pattern at 117 K is the same as that at 48 K, albeit much weaker, and the striped domains that show up on cooling do not make an appearance.

The fading away of the ferromagnetism on warming warrants further study, so I developed a scheme to quantify the ferromagnetic moments from the PEEM images and create a magnetization curve. Taking the average contrast from each image is insufficient, as in the images with ferromagnetic domains in figure 2.3 (most clearly in the image taken at 48 K), there are two grayscales present: most of the image is black or white, but there are regions of light gray and dark gray. The reason for this is that the sample is twinned and the XMCD contrast is proportional to \( m \cdot k \), where \( k \) is the wavevector of the incoming x-rays. Magnetic domains from different twin domains have magnetizations along different axes, and thus and different XMCD contrast for the same magnetization. To compensate, I used the lowest temperature image from each cooling/warming cycle as a baseline. To generate a point at temperature \( T \), I divided the image taken at \( T \) by the coldest image pixel-by-pixel. I ignored the pixels in the domain walls in the coldest image, as the ratios were dominated by noise, and I took the absolute value of the ratios to account for magnetization flips.
Figure 2.3: The evolution of magnetic domains in La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ one cooling/warming cycle. (a) overview, showing thermal hysteresis. (b) the nucleation of ferromagnetic domains on cooling. (c) the disappearance of the ferromagnetic domains on warming, with enhanced contrast compared to the other two subfigures. The spatial scale is the same for all images.
Figure 2.4: The magnetization of LPCMO as a function of temperature, as determined by the PEEM images. Different symbols represent different cooling/warming cycles; squares correspond to the images in figure 2.3. An explanation of how I generated this plot is in the text.

I then made a histogram, which I fitted to a gaussian. In figure 2.4, I have plotted the locations of the peaks of the gaussians. The range of the plot is from 0 to 1, as the coldest image has the highest magnetization. The plot contains data from three cooling/warming cycles taken at two different areas on the sample, and I used a different marker for each. Squares correspond to the images in figure 2.3. As I will discuss later, the unconventional temperature dependence of magnetization below $T_C$ is due to interactions between the ferromagnetic and antiferromagnetic regions.

The RSXS measurements of the orbital and antiferromagnetic order are summarized in figure 2.5. The triangles show data taken during traditional warming and cooling scans. There is a complex hysteresis, where the intensity and correlation length curves cross each other, so we wanted to see what happened on cooling from a point where the signal is strongest and the correlation length in maximized. To achieve that, we cooled the sample to 32 K, then warmed to 150 K. The diamonds show a cooling scan taken from that point. In addition to the unusual crossing curves, each scan resulted in a different value for $T_C$. Also, the behavior of the correlation
Figure 2.5: (a) RSXS intensity, (b) correlation length of the OO/AF domains, and (c) $q$ position of the RSXS peaks. (▲) warming; (▼) cooling from room temperature; (♦) cooling, after warming from 32 K to 150 K.
length is unconventional above $T_C^1$: on warming, it rises until it goes through the shaded region marked $T_g$, and on cooling, it is constant below that region, never reaching the value that it reaches on warming.
2.2. COMPETING ELECTRONIC ORDER IN LPCMO

2.2.2 Glassy Superlattice Order as an Explanation

These phenomena can be explained if the superlattice order is glassy, locking in lattice distortions and thus inhibiting the evolution of electronic order. There is evidence of freezing on the cooling scan, as the correlation length is constant between \( T_g \) and \( T_C \). Were there not, the correlation length would reach the same value that it reaches on warming. The glass transition is not a sharp transition, so I have labeled a range of temperatures \( T_g \) to show the range in which the freezing/melting takes place. When the ferromagnetism sets in, there is still lattice strain from the charge and orbital order, which is reflected in the striped domains present above 71 K in the images in figure 2.3b. Ferromagnetism slowly becomes more stable, and the lattice reverts to an unstrained state once the it dominates, with small regions of superlattice order remaining. On warming, the ferromagnetism inhibits lattice strain, so \( T_C \) is much higher than on cooling. The charge/orbital/antiferromagnetically ordered domains grow substantially at \( T_C \), and the strain does not freeze until they reach larger sizes than they reached at any point on cooling\(^2\). Interestingly, the correlation length appears to increase as the temperature is increased further, until \( T_g \). This would be absurd, and the explanation for this is that the domains are not all the same size, so the measured correlation length is close to the average correlation length of the domains. As illustrated in figure 2.6, the smaller domains melt at a lower temperature, resulting in a larger apparent correlation length. Eventually, the glass melts, and the domains shrink and disappear.

The interplay between the ferromagnetism and the glassy superlattice order near and below \( T_C \) is a critical component of CMR, so I will discuss it in depth. The ferromagnetic moment has a very unconventional temperature dependence, and this can be understood if the superlattice order is still glassy below \( T_C \). The key to understanding the interaction is the accommodation strain, which buffers the unstrained

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\(^1\)I focus on the correlation length rather than the integrated intensity because the latter is proportional to both the sample coverage of the superlattice order and to the order parameter, which increases with decreasing temperature. These two quantities cannot be easily disentangled.

\(^2\)The freezing is still likely a fast process, so time-dependent measurements of this phase transition would be extremely interesting, but also extremely difficult: even if the sample could be heated by a laser in a pump-probe setup, the thermal hysteresis makes recovering the initial state extremely time-consuming.
ferromagnetic metallic regions and the strained regions of superlattice order. As the sample cools, the ferromagnetism invades the regions of accommodation strain, forcing them closer to the structure of the unstrained regions. The plot of the superlattice $q$ versus temperature in figure 2.5c elucidates this point. Above $T_C$, $q$ is constant, as the paramagnetic insulating phase does not interfere with the accommodation stain. The continuous shift in $q$ below $T_C$ means that the lattice constants within the strained region are changing. This weakens the electronic order present there, as illustrated in figure 2.7. At very low temperatures ($< 25$ K), there have been reports of yet another glass transition [45, 44, 46]. This transition is thought to occur in the accommodation stain, so it represents an overall freezing of the lattice: below this transition, the ferromagnetic metallic phase is no longer able to force the accommodation strain to relax. That the superlattice order remains to a low temperature shows that it is somehow inherently stable, and the source of that stability remains the biggest question in CMR.

As Phan et al. [34] showed, an applied field is enough to melt the superlattice order. Below 75 K, subjecting LPCMO to an applied field of 5 T is sufficient, as evidenced by the much faster rise in magnetization when the field is turned on for a second time. This means that the phase separated state is not the ground state; as one might expect, a purely ferromagnetic metallic phase is more favorable. Most CMR measurements have been done by ramping the temperature in a fixed applied field, so in that case what is likely happening is that the field weakens the superlattice order, so it has a smaller effect on the ferromagnetic metallic phase than in no applied field. Once the ferromagnetic metallic phase forms, it has a lower resistivity than in the zero field measurement. Also, in ferromagnetic metallic manganites, CMR is highest near $T_C$, mostly due to the increase in $T_C$ upon application of a magnetic field.

Also of great importance is the phase transition from the charge/orbital ordered and antiferromagnetic phase to the ferromagnetic metallic phase. As I discussed above, ferromagnetism forms in a strained environment before completely taking over on cooling. The crossing hysteresis provides a way to investigate this further, as the system is in different configurations above $T_C$ for warming and for cooling. The
configuration on warming is more energetically favorable, as it forms out of the unstrained lattice at $T_C$, generates more RSXS intensity, and has ordered regions with larger correlation lengths. Comparing what happens when cooling from these two configurations, we see that $T_C$ is lower in the cooling-from-warming scan than in the traditional cooling scan. From the behavior discussed in the preceding paragraphs, we know that ferromagnetism becomes relatively more energetically favorable as the temperature is lowered. Thus, the larger charge and orbitally ordered domains observed in the warming-to-cooling scan are more stable — they are either a more durable glass or in a lower energy state — than the smaller domains observed in the traditional cooling scan. This shows that the superlattice order completely controls the phase transition into the ferromagnetic metallic phase. Furthermore, its glassy nature prevents the lowest-energy ground state, whether it be even larger charge and orbitally ordered domains or weak ferromagnetism, from forming.
CHAPTER 2. ELECTRONIC ORDER IN $La_{0.35}Pr_{0.275}Ca_{0.375}MnO_3$

2.3 Types of superlattice order present

Beyond the quantities pictured in figure 2.5, we can use RSXS to measure a resonance profile, which is the dependence of the scattered intensity on photon energy. For superlattice order, there is significantly more information present in the resonance profile than in an x-ray absorption scan because, as I discuss in section 1.2.3, most of the terms in the scattering cross section cancel out. Those that are left correspond only to the superlattice order, which is responsible for the entire scattering signal. As first shown in [30], resonance profiles from orbital order and from antiferromagnetism look extremely different, so they can be used to determine exactly which type of order is present.

An overview of the temperature dependence of resonance profiles in LPCMO is shown in figure 2.8. On crossing $T_C$, the lineshape changes dramatically. Above $T_C$, there are small variations in the lineshape as well. While they may be a sign of subtle changes in the electronic order, the difficulty in interpreting manganese resonance profiles precludes any more in-depth analysis. What is clear is that there is no sudden change above $T_C$, which would be associated with the antiferromagnetic transition temperature $T_N$, so it is safe to say that for LPCMO, $T_N = T_{CO/OO}$. I instead focused my efforts on the large change that occurs at $T_C$.

Our measurements relied on twinning within the single crystal of LPCMO. Figure 2.9 illustrates the implications of this twinning. Most importantly, it results in the overlap of the $(1\frac{1}{2}0 0)$ and $(01\frac{1}{2}0)$ superlattice peaks, so that they can be measured in the same experimental geometry. In addition, $a \neq b$, so the magnitude of $q$ is slightly different for the two superlattice peaks. The difference was not enough to allow for the two superlattice peaks to be individually resolved in momentum scans, so we measured resonance profiles on either side of the peak in $q$, where the relative contributions of orbital order and antiferromagnetism are different.

Figure 2.10 shows the results of these measurements. We optimized $q$ and the energy, and then took resonance profiles at the $q$ values where the scattered intensity was maximized, which I will refer to as $q_0$; and at the points where the intensity was half the peak value, which I will refer to as $q_<$ and $q_>$. At 160 K, above $T_C$,
2.3. TYPES OF SUPERLATTICE ORDER PRESENT

Figure 2.8: Temperature series of LPCMO resonance profiles, warming (top) and cooling (bottom). Each is normalized to its peak value, and there is a vertical offset between curves. Red curves were taken above $T_C$, as determined by the measurements in figure 2.5, while blue curves were taken below $T_C$. 
Figure 2.9: Top left: the idealized picture of CE type orbital and magnetic order present in many manganites, including LPCMO. Note that OO and AF show up at different values of $q$: OO modulates along the $b$ axis and thus shows up at $q = (0 \frac{1}{2} 0)$, while AF modulates along the $a$ axis and shows up at $q = (\frac{1}{2} 0 0)$. Top center: the twinned orientation. Our sample is crystallographically twinned, so both orientations shown are present. Bottom left and center: the relevant superlattice diffraction peaks in reciprocal space. $a < b$, so the magnitudes of $q$ are different for the two peaks. Bottom right: the measured signal is a superposition of the normal and twin regions.
the resonance profile has a dramatic $q$ dependence. Interestingly, the lineshape at $q_>$ looks like those in measurements of other compounds taken above $T_N$, where only orbital order is present [30, 35], so I will attribute it to orbital order. At $q_<$, the peak at 639.8 eV is strongest relative to the other peaks. A peak at this energy is a signature of antiferromagnetism [30, 29, 35]. In compounds where $T_{CO/OO} > T_N$, such as the Pr$_{1-x}$Ca$_x$MnO$_3$ series, the peak shifts to a higher $q$ when antiferromagnetism is present [30, 29, 35], consistent with the illustration in figure 2.9. My measurements seem to imply the opposite.

There are a few possibilities for this discrepancy. One is that the model of CE type order shown in figure 2.9 is incorrect, but that would contradict years of measurements, so it can be ruled out. Another is that the orbital order and antiferromagnetism in LPCMO above $T_C$ is different from the CE type order present in those other compounds. This is a hard case to make, though, and there is no compelling reason to do so. More likely is that there are multiple types of superlattice order present in LPCMO. This is an attractive possibility for a few reasons. The difficulty in simulating resonance profiles in manganites, as compared to other materials, implies that CE type order is not the whole story. Furthermore, it does not contradict previous measurements [9, 30, 35, 29] that found that for $T_N < T < T_{CO/OO}$ (only charge and orbital order preset), the scattering peak is at a lower $q$ than it is for $T < T_N$ (antiferromagnetism present as well), as they showed a shift in $q$ between different regimes of superlattice order, not details within one regime. Finally, as I will discuss below, it could have a similar explanation to the unexpected results from below $T_C$ in LPCMO.

A schematic of the possibility of multiple types of superlattice order is shown in figure 2.11. The main idea of this model is that different degrees of lattice distortion are hospitable to different types of superlattice order. Orbital order induces lattice distortions, which bring with them accommodation strain. The distortions are maximum in the red region in the figure, and this region likely corresponds to the CE type order illustrated in figure 2.9. Between that order and the undistorted lattice (green) is a finite region of accommodation strain (blue). Within the accommodation strain, there may be superlattice order—nothing is precluded. Given the strong coupling
Figure 2.10: (a) An x-ray absorption spectrum taken at 160 K. (b) $q$ and (c) energy dependence of the $\left(0 \frac{1}{2} 0\right)/\left(\frac{1}{2} 0 0\right)$ peak intensity at 160 K on warming, which is above the $T_C$. The data were taken at $E = 642.2 \text{ eV}$ and $q_0 = 0.5788 \text{ Å}^{-1}$, respectively. The arrows in (b) indicate the values of $q_{<}, q_0$, and $q_{>}$, where we measured the energy dependence, and the arrow in (c) indicates the energy at which we measured the $q$ dependence. (d), (e) the same as (b), (c), but at 50 K on cooling, just below $T_C$. The data were taken at $E = 642 \text{ eV}$ and $q_0 = 0.5752 \text{ Å}^{-1}$, respectively. All data in this figure were taken with $\pi$ polarized incoming light.
2.3. TYPES OF SUPERLATTICE ORDER PRESENT

Figure 2.11: A schematic for the possibility of multiple types of superlattice order in LPCMO. The red region exhibits the highest degree of lattice distortion, and is likely CE type charge, orbital, and antiferromagnetic order. The blue region is accommodation strain, with a lattice that is less distorted than in the red region, stabilizing a different type of superlattice order.

between order within the lattice and electron systems, it stands to reason that the most stable electronic order within the accommodation strain is fundamentally different from that in the maximally distorted regions. Because lattice distortions cause local changes in lattice constants, regions with different degrees of lattice distortions generate superlattice reflections at slightly different values of \( q \), so the changes in resonance profiles as a function of \( q \) are a result not of twinning but of the nonuniformity of lattice constants. It is unclear whether the superlattice order within the accommodation strain generates a plateau in lattice constants as a function of position or the order exists over a region of constantly changing lattice constants. A full evaluation of this scenario of superlattice order requires calculations and measurements that are beyond the scope of this dissertation.

Below \( T_C \), the picture is completely different. The resonance profile does not depend on \( q \). It exhibits features that would imply antiferromagnetism based on the arguments above, which presents an opportunity to perform more thorough measurements as a check on this analysis. Specifically, the well-known relationship between the polarizations of the incoming and outgoing x-rays and the directions of the magnetic moments [28] can be measured using an azimuthal rotation scan. The relevant
parameters are all illustrated in figure 2.12. As I discussed in section 1.2.3, the relevant term in the scattering factor is

\[ f''_{\text{mag}} = (\hat{\varepsilon}' \times \hat{\varepsilon}) \cdot \hat{m} F^{(1)} \]  

(2.1)

Hill and McMorrow [28] break the incoming and outgoing polarization into \( \pi \) and \( \sigma \) components and calculate the polarization-dependent scattering factors to be

\[ f_{\sigma \rightarrow \sigma'} = 0 \]  

(2.2)

\[ f_{\sigma \rightarrow \pi'} \propto - \hat{k}' \cdot \hat{m} \]  

(2.3)

\[ f_{\pi \rightarrow \sigma'} \propto \hat{k} \cdot \hat{m} \]  

(2.4)

\[ f_{\pi \rightarrow \pi'} \propto (\hat{k}' \times \hat{k}) \cdot \hat{m} \]  

(2.5)

If the order is indeed magnetic, then determining the direction of \( \hat{m} \) is a question of trial and error. Since I already know the answer, I will rewrite the scattering factors
2.3. TYPES OF SUPERLATTICE ORDER PRESENT

for $\mathbf{m}$ along the $c$ axis:

$$f_{\sigma\rightarrow\sigma'} = 0 \quad (2.6)$$
$$f_{\sigma\rightarrow\pi'} \propto -\cos \theta \sin \psi \quad (2.7)$$
$$f_{\pi\rightarrow\sigma'} \propto -\cos \theta \sin \psi \quad (2.8)$$
$$f_{\pi\rightarrow\pi'} \propto \sin 2\theta \cos \psi \quad (2.9)$$

The measured intensity is proportional to $|f|^2$. In addition, there was no polarization analysis of the scattered x-rays, so I will add the intensity contributions from $\sigma'$- and $\pi'$-polarized scattered photons. The result is

$$I_\sigma \propto \cos^2 \theta \sin^2 \psi \quad (2.10)$$
$$I_\pi \propto \cos^2 \theta \sin^2 \psi + \sin^2 2\theta \cos^2 \psi \quad (2.11)$$

These curves are plotted along with the data in figure 2.13. The match is as good as can be expected. Of interest is why the superlattice order changes at $T_C$. A likely scenario is that this antiferromagnetism is exactly what exists in the accommodation strain above $T_C$ (blue regions in figure 2.11). The correlation length of superlattice order is much lower below than above $T_C$, so there may not be enough space for accommodation strain to build up to the point where CE type order is favorable. Thus only the order that exists within the accommodation strain above $T_C$ is able to exist below $T_C$. This is supported by the similarity of the resonance profiles taken above $T_C$ at $q_<$ and below $T_C$ and $q_0$, which are plotted in figure 2.14. The differences, which are especially strong at the $L_2$ edge, are due to the coexistence of orbital order above $T_C$. These measurements lead to a clearer picture of the superlattice order present in manganites, which is essential for an understanding of why there is glassy behavior in the first place.
Figure 2.13: The azimuthal dependence of integrated RSXS intensity in LPCMO at 50 K for incoming $\sigma$- and $\pi$-polarized photons. The curves are the functions in equations 2.10 and 2.11.

Figure 2.14: A comparison of the resonance profiles measured at $q_<$ above $T_C$ and at $q_0$ below $T_C$. Each is normalized to its maximum intensity.
Chapter 3

Inhomogeneities in Bi-Layered La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$

The unusual electronic properties of mixed-valence manganites have unsurprisingly generated interest in their band structure. The best experimental method for measuring it is angle resolved photoemission spectroscopy (ARPES), which measures both the energy and momentum of photoelectrons. ARPES is extremely surface sensitive, so the sample surface must be clean. The only way to achieve this is if the surface never comes into contact with air, so ARPES requires either growing or cleaving the sample in the ultra high vacuum environment required for the experiments. Growing a sample in situ is difficult, so ARPES is generally restricted to materials that cleave easily. For manganites, this means going to a layered system. ARPES does not work on highly insulating systems due to space charge, and manganites with a ferromagnetic metallic ground state are the most interesting to measure anyways. The La$_{1-x}$Sr$_x$MnO$_3$ series of nonlayered compounds is the most favorable to the ferromagnetic metallic phase, so a natural choice of a layered system would be single-layered La$_{1-x}$Sr$_{1+x}$MnO$_4$. Unfortunately, the ferromagnetic metallic phase is suppressed in layered materials, so all compounds in the La$_{1-x}$Sr$_{1+x}$MnO$_4$ series are insulating. Adding a layer to form bi-layered La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ is sufficient for the formation of a ferromagnetic metallic phase, although it has a much higher resistivity than La$_{1-x}$Sr$_x$MnO$_3$. 
3.1 Inconsistent ARPES Results

ARPES measurements of La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ seem to have raised more questions than they have answered, as different measurements have produced seemingly inconsistent results. For electronic conduction, the most important aspect of the band structure is what it looks like around the fermi energy. In particular, the presence or absence of a quasiparticle peak tells us whether there are free charge carriers. In samples with $x = 0.36$, experimenters have measured a completely metallic band structure [36]. A later measurement [37] provided results inconsistent with those, showing pseudogapped band structure, with no intensity exactly at the fermi energy but a broad peak just below. At $x = 0.40$, which non-ARPES measurements show qualitatively has the same properties as $x = 0.36$, measurements have shown the pseudogap for all values of crystal momentum $k$ [38] and strong $k$ dependence of the quasiparticle peak [39].

There are also conflicting reports on the temperature dependence of the various phenomena that are observed. For $x = 0.36–0.4$, $T_C \sim 120–130$ K. ARPES measurements on $x = 0.40$ samples show a distinct change in the band structure at that temperature [38, 39], while a measurement on $x = 0.36$ shows that there is still spectral weight at $E_F$ at 185 K [36] and in $x = 0.38$, the spectral weight at $E_F$ disappears at 300 K [40]. Bulk magnetization measurements of $x = 0.40$ also showed magnetic transitions at both 120 K and 300 K [41].

These inconsistencies raise the question of what exactly is being measured. It has been posited that the exact behavior of La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ is extremely dependent on doping at this doping range [40], but the similar physical and magneto resistive properties of all of these materials seem to indicate otherwise. Another possibility is that the single crystals are spatially inhomogeneous. This is more likely to happen in layered manganites than in perovskite manganites because there are two ways to follow an (La,Sr)O monolayer: either with an MnO$_2$ monolayer, which happens within the bilayered structure (or, in the perovskite manganites, after every (La,Sr)O layer), or with another (La,Sr)O layer, as occurs between the bilayered structures. Current growth methods allow for very high quality bilayered manganites to be grown, but
3.1. INCONSISTENT ARPES RESULTS

Figure 3.1: A schematic of bi-layered $\text{La}_{2-x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ with a stacking fault of septilayered $(\text{La,Sr})_8\text{Mn}_7\text{O}_{22}$ (in box)
that does not preclude the presence of “stacking faults,” where over a small region, a MnO$_2$ layer takes the place of a second (La,Sr)O layer. This scenario is illustrated in figure 3.1. There is a clear trend among layered La$_{n(1-x)}$Sr$_{1+n_2}$Mn$_n$O$_{3n+1}$ with $x = 0.4$ where the materials become more metallic with increasing $n$. Single-layered La$_{0.6}$Sr$_{1.4}$MnO$_4$ is highly insulating, bi-layered La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ is a bad metal, and cubic ($n = \infty$) La$_{0.6}$Sr$_{0.4}$MnO$_3$ is very metallic [42], with a much higher $T_C$ than the $n = 2$ compound. Thus, stacking faults would appear to be more metallic, and would result in higher ARPES intensity near the fermi energy.

### 3.2 Imaging Stacking Faults in PEEM

If there are indeed spatially inhomogeneities, they should be visible under a microscope. The first thing that we investigated was the anomalous magnetization present above $T_C$, which disappears around 300 K [41]. As shown in figure 3.2, there are small regions of the sample that have a higher $T_C$ than the sample as a whole. These regions explain the nonzero magnetization above $T_C$. As an aside, figure 3.3 shows an XMCD image taken at the oxygen edge. Oxygen generally does not exhibit XMCD, so this shows that there is a strong magnetic interaction resulting from the hybridization between the oxygen 2$p$ and manganese 3$d$ states orbitals. The accompanying spectrum shows that the dichroism is confined to the pre-edge feature that represents that hybridization [24].

The next step is to establish that the regions that are ferromagnetic above $T_C$ are indeed stacking faults. The proper tool for this is the dependence of x-ray absorption on the direction of the polarization of linearly polarized light, which is known as linear dichroism. The oxygen edge is the logical place to do this, because the oxygens between layers (such as those at the top two and bottom two rows of figure 3.1) have one manganese nearest neighbor and one lanthanum/strontium nearest neighbor, while those within layers have two manganese nearest neighbors. Park et al. showed that this leads to linear dichroism in the oxygen spectrum, concentrated at a feature that they associate with oxygen-lanthanum/strontium hybridization [24]. Figure 3.4 shows that there is no linear dichroism in the regions that are ferromagnetic above
3.2. IMAGING STACKING FAULTS IN PEEM

Figure 3.2: XMCD images of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, taken at (a) $T = 115$ K (below $T_C$), (b) 121 K (just above $T_C$), and (c) 310 K (well above $T_C$). All images depict the same region of the sample.

$T_C$, while it is strong elsewhere in the sample. This is a clear indication that those regions are stacking faults. The lack of linear dichroism does not necessarily mean that they are cubic: the PEEM’s probing depth is only a few nanometers, so it is possible that the first rock salt (La,Sr)O layer below the surface in the stacking fault is deep enough that it does not make a large contribution to the x-ray absorption signal.

The existence of stacking faults shows that ARPES measurements were not performed on at pure $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, but in a region of a couple hundred microns in both directions, we saw only a few stacking faults, each similar in size to the one in figure 3.2. One possible explanation is that the density of stacking faults varies from sample to sample, and we measured one with an abnormally low density. Another is that within a sample, there are regions of varying stacking fault density. ARPES samples need to be cleaved in situ, and the quality of the surface varies from cleave to cleave, and even within a single cleave. Quasiparticle peaks show up only on a good cleave, so a quasiparticle signal that is not uniform across the sample surface is not seen as unusual, and experimenters perform measurements where the quasiparticle signal is strongest. Thus, it is not surprising that there are a large number of reports
Figure 3.3: (a, b) XMCD images taken at the manganese and oxygen edges, respectively, at 15 K. The faint hexagonal features visible at the center left of (a) are artifacts from the fiber bundle that carries the PEEM image from the phosphor screen to the CCD. (c, d) spectra averaged over the regions indicated by boxes in (a, b). Intensity is the sum of the spectra from images taken with left- and right-hand circular polarization, while XMCD is the asymmetry. The arrows indicate the energies at which the images in (a, b) were taken.
3.2. IMAGING STACKING FAULTS IN PEEM

Figure 3.4: (a) geometry of the linear dichroism measurements, showing the crystallographic $c$ axis and the two linear polarizations. $\pi$ polarization makes a 30° angle with the $c$ axis while $\sigma$ polarization, which points into and out of the page, is entirely in the $ab$ plane. (b) The same image from figure 3.2b, just above $T_C$. (c, d) Spectra of the stacking fault and a bi-layered region, respectively. The boxes do not represent the boundaries of the regions measured; to obtain the stacking fault spectrum, we averaged over only the stacking fault itself. The arrows indicate a feature that is related to O-(La,Sr) hybridization and exhibits a high degree of linear dichroism in layered systems [24].
of quasiparticles in ARPES measurements of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$.

### 3.3 Interactions Across Stacking Fault Boundaries

Another topic of interest is the magnetic interactions between the stacking faults and the bilayered host. In polycrystalline samples, there is little correlation between the magnetism of neighboring grains \cite{43}, but despite their different crystal structure, the stacking faults are not truly independent grains. They are formed using the host crystal as a template, as shown in figure 3.1. In particular, since their $T_C$ is much higher than that of the host, they may act as pinning sites for magnetization when the sample is cooled through the host’s $T_C$.

Figure 3.5 shows PEEM images taken around $T_C$ on cooling. Unfortunately, the
3.3. INTERACTIONS ACROSS STACKING FAULT BOUNDARIES

A temperature diode was not connected properly for these measurements, but estimates based on a comparison the XMCD contrast of these images with others taken when we had proper temperature readings indicate that the sample cooled by about 15 K over the course of the measurement. The first image is taken above the host’s $T_C$, and it shows a stacking fault that is magnetized up (white) surrounded by the non-magnetic (gray) host. As the sample is cooled, magnetism sets in everywhere. In particular, note that in the image taken at $t = 210$ s, the area around the stacking fault is spin up, resulting in a curved domain wall around it. Eventually, the nearby spin down domain in the host encircles the stacking fault and, in the process, the stacking fault switches.

This has two important implications. The first is that the stacking fault and host have strong magnetic interactions. As I showed in section 1.1.1, ferromagnetism in manganites is strongly tied to the hopping of $d$ electrons between manganese sites. The magnetic interactions show that this hopping happens between the stacking faults and the host crystal, despite the different structure and chemical composition of the two compounds. The second implication of this is that the stacking faults do not act as pinning sites for the magnetization. Around the host’s $T_C$, the magnetization of the stacking faults is much stronger than that of the host, so one would expect that the stacking faults would act as pinning sites, with the host would unable to switch them. Looking at the sequence from 350–435 s, it is clear that that is not the case, as the stacking fault switches from spin up to spin down as the spin down domain forms around it in the host. This means that there is a significant overlap of the wavefunctions of the delocalized $3d$ electrons in the host and in the stacking fault. A more systematic measurement of this phenomenon over stacking faults of many sizes could provide experimental insight into the spatial extent of these wavefunctions.
Chapter 4

What next?

This dissertation describes progress toward an understanding of mixed-valence manganites, but there is still much to learn. In this chapter I will go through a few open questions and possible future experiments.

4.1 Open Questions

Why is there glassy behavior in manganites? This is really the key question of mixed-valence manganites. For a while, the question has been “how can the ground state consist of multiple competing phases?” but as I detailed in chapter 2, recent experiments, including mine, suggest that this is a false premise: the phase separated state that exists at zero magnetic field is not the ground state but instead the result of the glassy nature of the superlattice order. There is also glassy superlattice order above $T_C$ in LPCMO, La$_{0.7}$Ca$_{0.3}$MnO$_3$ [16] and La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ [32], and there is a glass transition around 25 K in La$_{0.625-y}$Pr$_y$Ca$_{0.375}$MnO$_3$ [44, 45, 46], which I discussed in chapter 2.

There is not a solid explanation as to why all of these glasses occur. One early theory explaining glassy behavior in manganites was disorder of the A-site ions: when the various species used are of very different radii, there is natural disorder in the lattice, leading to a spin glass ground state [47, 48]. The idea was that in systems where the A site ions were approximately the same size, there was “quenched disorder”
and thus no reason for a glass to develop. The La\(^{3+}\) and Ca\(^{2+}\) ions are almost exactly the same size, and Pr\(^{3+}\) is only slightly smaller, so the aforementioned glasses in \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) and in \(\text{La}_{0.625-y}\text{Pr}_y\text{Ca}_{0.375}\text{MnO}_3\) show that glassy behavior exists in systems with quenched disorder.

Disorder may still be responsible, although it is likely not related to the A site ions, as scanning electron diffraction measurements of \(\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3\) have shown that the superlattice order that coexists with the ferromagnetic metallic phase is not pinned to defects or inhomogeneities because it shows up in different locations on different cooling cycles [27]. At this point it is not clear where else disorder might come from. Another challenge in finding an explanation is the difficulty of modeling glasses, which are by definition not at equilibrium. The most successful theoretical studies of manganites have been computational in nature, and even current supercomputers lack the computing power to perform calculations on large enough clusters to capture long-range ferromagnetism and superlattice order [49, 50]. Without a simplified model that is significantly less computationally intensive, a true theory for glassy behavior in manganites is many years out.

**What properties of manganites are universal?** Mixed-valence manganites are a veritable alphabet soup of chemical formulas\(^1\), so there is the natural temptation to simplify the picture of what is happening by equating phenomena seen in compounds with similar properties. This is made difficult in part because as composition changes, properties sometimes change sharply, as they do in the \(\text{La}_{1-x}\text{Ca}_x\text{MnO}_3\) when \(x\) crosses 0.5, and sometimes slowly evolve, as they do when \(y\) is varied in \(\text{La}_{0.625-y}\text{Pr}_y\text{Ca}_{0.375}\text{MnO}_3\) series. For example, in this dissertation, I posited that the glassy superlattice order that is present in \(\text{La}_{0.35}\text{Pr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3\) above \(T_C\) and causes the phase transition to the ferromagnetic metallic phase to be first order is the same phenomenon as the glassy polarons that are present in \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) and \(\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\) above \(T_C\) and causes the phase transition to the ferromagnetic metallic phase to be first order. This is not straightforward, because the charge, orbital, and

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\(^{1}\)This is without considering thin films, which have different properties from bulk single crystals of the same compounds and even other thin films on different substrates or with different thicknesses.
antiferromagnetic order that appears above $T_C$ in $\text{La}_{0.35}\text{Pr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3$ is also the ground state of a number of non-ferromagnetic manganites, which are (for good reason) seen as distinct from the ferromagnetic metallic manganites, and the idea that a phenomenon that is known to exist in the latter is really a manifestation of something that defines the former is not straightforward, even though $\text{La}_{0.35}\text{Pr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3$ exhibits both the former and the latter.

Further compounding the issue is the instinct that is common among scientists to ascribe an unusual new measurement that does not fit with one’s notions of how manganites work to special complexities within the specific compound measured. An extreme example of this is the ARPES measurements on $\text{La}_{2-x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ for $x = 0.36–0.40$, which I discussed in section 3.1, where compounds which qualitatively have exactly the same bulk physical properties are said to have very different electronic structure. A cynical view would be that this is due to a desire to conduct more and more experiments on manganites, as the problem will never be “solved,” but I think that what is happening is merely the confusion of conclusions reached in the literature (which are easy to remember) with measurements (which are harder to remember and may lead to conclusions different from those reached by the people who performed them), along with the fact that it is impossible to perform every possible measurement on every possible system. The result is that everybody working on manganites has a slightly different picture of the materials in their heads, and it is much easier to keep one’s own picture consistent with new results if the aspects of manganites that are thought to be universal are kept to a minimum, or if compounds that straddle the boundaries, such as $\text{La}_{0.35}\text{Pr}_{0.275}\text{Ca}_{0.375}\text{MnO}_3$, are viewed as having special properties, such as the low-temperature kinetic arrest, that prevent them from being compared to compounds on either side of the boundary. I would argue that such complexities are either not observable or not present in compounds where only one type of long-range order is present and arise from the balance between the ordered phases in $\text{La}_{0.625-y}\text{Pr}_y\text{Ca}_{0.375}\text{MnO}_3$.

Now that I have stated the question and the difficulties behind resolving it, what is the quickest way to reach a convergence? The most logical answer would be simulations, because people who run them can continuously vary parameters much more
finely (and predictably) than can any crystal grower, resulting in a clear picture of what evolves into what and thus determines what is truly universal. The only issue is that the aforementioned limitations on the sizes of clusters that can be simulated limit the use of simulations in picking up on the subtleties that are necessary to draw these conclusions. The best hope, then, is to conduct experiments that will demonstrate this smooth evolution or a lack thereof. A combined resonant elastic soft x-ray and neutron scattering study through the La$_{0.625-y}$Pr$_y$Ca$_{0.375}$MnO$_3$ series will be able to do just that, as well as make comparisons with the insulating Pr$_{1-x}$Ca$_x$MnO$_3$ series. The only issue I see is finding people who are motivated enough and can grow enough samples and obtain enough beamtime to attempt such an undertaking.

**How does this all relate to colossal magnetoresistance?** I have done plenty of hand waving, but this requires a model to be answered properly. While some detailed simulations have been able to reproduce CMR [49], tying glassiness to CMR requires a much simpler model that can describe large systems. The formalism for this model does not currently exist, but I think that creating such a model is the most important theoretical problem in manganites today.

### 4.2 Future Experiments

These experiments will not provide direct answers to the questions above, which are more related to modeling, but they are important in that they will tell us what kinds of behavior our models have to be able to reproduce. For the most part they are in development or have begun but not yet yielded comprehensive results.

**Resonant coherent imaging of La$_{0.35}$Pr$_{0.275}$Ca$_{0.375}$MnO$_3$ in reflection** The ideal manganite imaging experiment would be able to distinguish regions with superlattice order, regions with ferromagnetic order, and regions with neither. The reason that nobody has performed this measurement is that existing microscopy methods that are sensitive to one type of order are not sensitive to the other. A possible
solution to this problem is to use resonant coherent imaging, where an x-ray scattering pattern taken with a coherent beam can be used to produce a real-space image [51, 52]. The technique has been used mostly in the transmission geometry, and has provided images of ferromagnetic domain structures [53, 54]. Transmission means scattering angles of a few degrees at most, while the only way to unambiguously measure superlattice order using x-ray scattering is to go to the Bragg peak, which is around \( \theta = 63^\circ \) for LCPMO, so the technique needs to be adapted for measurement in reflection. The main difficulty is that the scattered intensity is much higher at small scattering angles, so even at a superlattice peak the signal is much weaker in reflection. There have been coherent scattering studies of the superlattice peak in \( \text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3 \) [55, 56], which have shown that the domain structure of the superlattice order is extremely stable over time. Imaging is more challenging, but the technique was recently demonstrated on a sample with a test pattern [57]. Going from a test pattern which had the advantage of elemental contrast to an intrinsic superlattice peak that has much weaker contrast and only occurs well below room temperature is not trivial, but the pieces are coming into place. As for the ferromagnetism, techniques used in transmission should work for reflection as well. LPCMO is the ideal material for these experiments for the same reason it was ideal for mine: both the superlattice order and ferromagnetism generate relatively strong signals, and the best material in which to study phase separation is one where both competing phases are strong.

**Resonant elastic soft x-ray scattering in a magnetic field** An electron microscope such as PEEM is inoperable in a high magnetic field, but scattering measurements are still possible. I have shown that the behavior of LPCMO is driven by the superlattice order and lattice distortions, so a measurement of the superlattice order as a function of magnetic field is more important than images of the ferromagnetic domains anyways. Thus, this measurement will provide key experimental evidence about the nature of the CMR transition. There is a beamline at BESSY in Berlin with a scattering chamber that can reach 6 T [58], and a new high-field scattering chamber at the Advanced Light Source coming online soon.
4.2. FUTURE EXPERIMENTS

ARPES of cubic, non-layered manganites  This is the most difficult of the experiments that I propose here. The main motivation is that La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ is at best a bad metal, with relatively low conductivity, so measurements of cubic manganites would provide a much better picture of the band structure. Also, a much larger range of compounds could be measured. As I mentioned in chapter 3, the reason that bilayered manganites have been favored for ARPES is that they can easily be cleaved in situ, so measurements can always occur on a fresh surface. Cubic manganites cannot be cleaved, but there are two ways to get around this. The first is somewhat stochastic: basically, it calls for performing ARPES on only stacking faults. Samples can be screened with a simple measurement of magnetization versus temperature in a magnetic field, as a relatively high ratios of magnetic moment above the nominal $T_C$ to the magnetic moment below $T_C$ is an indication of a sample with a high stacking fault density. Measuring only a stacking fault is somewhat of a challenge given the relatively large beam sizes, but systems with beam sizes small enough to isolate stacking faults are in development [59]. The downside of this scheme is that the stacking faults need to be within a bilayered system which itself has a high enough conductivity for ARPES to work, and only La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ meets this criterion, so only La$_{1-x}$Sr$_x$MnO$_3$ could be measured. The other option would be to attach a sample growth chamber to the ARPES chamber so that samples never need to be removed from vacuum. This would be easiest with a pulsed laser deposition or molecular beam epitaxy system, both of which are used primarily to grow thin films. Then, practically any metallic manganite could be measured. The major downside to this is that it requires the ARPES system to be attached to a well-characterized thin film growth chamber, but such a system is in development [59].
Bibliography


been quenched a couple of times, so 5.9 T is currently the maximum recommended field.