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LOCAL ATOMIC STRUCTURE AND THE METAL-INSULATOR TRANSITION OF $La_{1-x}Ca_xMnO_3$

By

Remo Giovanni DiFrancesco

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

LOCAL ATOMIC STRUCTURE AND THE METAL-INSULATOR TRANSITION OF $La_{1-x}Ca_xMnO_3$

By

Remo Giovanni DiFrancesco

 $La_{1-x}Ca_xMnO_3$ is one of a class of materials which were recently found to display Colossal Magnetoresistance. This has generated a great deal of interest in attempting to explain this phenomenon. Recent work has suggested that the lattice plays an important role in the electronic behavior of these compounds by way of the Jahn-Teller effect, leading to polarons. We have probed the lattice using atomic pair distribution functions, a local structural technique, to determine if changes in the lattice are present and how they correlate with the various electronic phases.

The structure is found to respond strongly to the metal-insulator transition with a distortion of the six oxygen atoms surrounding each Manganese site. We interpret this as the formation of polarons which are first seen in the ferromagnetic metallic (FM) phase and increase in density as the paramagnetic insulating phase is entered. The FM state is seen to contain two regions: a low temperature state in which all carriers are delocalized and the structure is undistorted, and a higher temperature area in which the delocalized charges coexist with polarons.

The FM state in the x = 0.5 material is found to contain a similar mixture of phases for a narrow range of temperatures. A charge ordering transition eventually suppresses the delocalized state which ultimately destroys the ferromagnetism. The PDF reveals that at high temperatures the carriers remain localized but their ordering is lost through an order-disorder transition. Multas per gentes et multa per aequora uectus aduenio has miseras, frater, ad inferias, ut te postremo donarem munere mortis et mutam nequiquam alloquerer cinerem. -Catullus

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Chapter 1

Introduction to Colossal Magnetoresistant Manganites

1.1 Introduction

This thesis deals with the local atomic structure of $La_{1-x}Ca_xMnO_3$ and how this affects its physical properties. First, early work on these materials from the 1950's is described. Interest in these materials was recently reawakened with the discovery of an extremely large magnetoresistance in thin films as we discuss in Section 1.1.2. The importance of the lattice, and in particular the local structure, to this phenomenon was predicted theoretically and verified experimentally as we describe in Section 1.1.3. In Section 1.2 we introduce different methods for measuring local structure including the atomic pair distribution function (PDF) technique, which is the approach we have used. The origin of the strong electron-lattice coupling is the Jahn-Teller effect which is introduced in Section 1.3.1. This results in lattice polaron formation which is briefly described in Section 1.3.2. Finally, we describe the structure and properties of the $La_{1-x}Ca_xMnO_3$ system which is the system studied in this work.

A number of recent reviews [3, 5] and collections [6, 7, 8] are available.



Figure 1.1: Basic structure of the perovskite cell. In $La_{1-x}Ca_xMnO_3$ the A and B sites are a random mixture of Lanthanum and Calcium. The oxygen sites form an octahedron about each Manganese.

1.1.1 Early work

In 1950 Jonker and van Santen [9] synthesized a series of manganese oxides of the general formula $A_{1-x}B_xMnO_3$, where A is a trivalent and B a divalent ion. These compounds form in the perovskite structure shown in Figure 1.1 in which the A, B, and Mn ions form interpenetrating simple cubic sublattices with O at the cubic faces and edges.

At finite doping values Mn takes on a mixed valence in order to preserve charge balance. A fraction of the ions, x, takes on a Mn⁴⁺ (d^3) state while the remainder are left in the Mn³⁺ (d^4) state. The doping level was found to influence the magnetic and electrical properties of these materials. For values of x close to 0 and 1 the ground state is antiferromagnetic while for intermediate (0 < x < 0.5) doping levels a ferromagnetic ground state was observed with a Curie temperature reaching its maximum at $x \approx 0.3$.

Subsequently, van Santen and Jonker [10] found that above T_c the resistivity was semiconductor-like, $d\rho/dT < 0$, while below T_c there is a transition to metallic



Figure 1.2: Resistivity vs. temperature curves for $La_{1-x}Sr_xMnO_3$ at various compositions. Note the large changes in slope near T_c for the intermediate-doped compounds [1].

behavior, $d\rho/dT > 0$, as well as a sharp reduction in resistivity as shown in Figure 1.2.

A mechanism called double exchange (DE) was proposed by Zener [11] to explain the coincidental appearance of metallicity and ferromagnetism. The essential ingredients of DE are that Mn is in a mixed valence state so that Mn^{3+} and Mn^{4+} are both present in the structure, that there is localized spin (in this case 3/2 spin) in the localized t_{2g} orbitals on each Mn ion, and that the t_{2g} holes are Hunds-rule coupled to the electron in a delocalized e_g orbital on the Mn^{3+} ions. Charge transport happens through the hopping of an e_g electron to an empty e_g orbital on a neighboring Mn^{4+} ion. The probability of hopping will depend on the relative alignment of the spins of neighboring Mn sites. Specifically, the hopping probability varies like $\cos \frac{\theta}{2}$, where θ is the angle between core-spins on neighboring Mn sites [12]. Therefore when the spins align ferromagnetically there is an enhancement in electron hopping.

The lattice does not play an important part in DE and the crystal structure received little attention until recently. Elemans *et al.* [13] published structural parameters from neutron diffraction for the series $La_{1-x}Ba_xMn_{1-y}Ti_yO_3$. The endmember $LaMnO_3$ was found to be highly distorted, with rotations and elongations of its oxygen octahedra. Although perovskites often show such rotations, the observed octahedral elongations were thought to be caused by the Jahn-Teller effect [14] which we will discuss in Section 1.3.1. With doping, these elongations seemed to vanish based on diffraction studies and the rotations decreased in magnitude. Overall, these materials remained of purely academic interest until the discovery of their magnetoresistance (MR).

1.1.2 Colossal magnetoresistance

Interest was reawakened with a series of experiments [15, 16] that studied the MR of these compounds associated with the transition from paramagnetic insulator (PI) to ferromagnetic metal (FM). They found large decreases in resistance when a field sufficient to drive the system into the FM region was applied. A much larger MR was found in thin films of several manganese oxides [17, 18, 19] which led to the term colossal magnetoresistance (CMR) to distinguish it from the previously discovered giant magnetoresistance (GMR). GMR is found in metallic multilayers with alternating layers of a ferromagnetic metal like Fe or Co, and normal metals like Cu with each layer being the thickness of the oscillation period of the RKKY interaction. GMR is created by reversing ferromagnetic domains defined by the layer thicknesses. The field strength needed to saturate the magnetoresistance is usually several tenths of a

Tesla, while a similar effect in CMR materials requires a field of over 5T.

It was found that the size of the MR effect is inversely related to T_c [20]. This can be understood quite easily. The large MR occurs because the sample is driven through an insulator-metal transition by the application of a strong external field. In the insulating (high-temperature) state the resistivity increases exponentially on cooling. At T_c the sample changes to a metal and the resistivity drops dramatically. If T_c is lower, the drop in the resistivity is larger simply because the resistivity of the insulating state is so high. The same argument can be applied to the case where the sample is driven metallic by an external magnetic field.

The T_c can be changed by varying the Mn⁴⁺ density, which changes the hole concentration and bandfilling. But we can also affect T_c by varying the bandwidth. This is done by changing the average size of the A ion in the ABO₃ formula which changes the lattice constant. In La_{0.7y}Pr_yCa_{0.3}MnO₃ and La_{0.7y}Y_yCa_{0.3}MnO₃ Hwang *et al.* [2] studied the evolution of T_c with the Ca-concentration, hence hole density, fixed. They found that as the average size of A, $< r_a >$, decreases, T_c also decreases (Figure 1.3).

Instead of creating internal pressure by changing $\langle r_a \rangle$, external hydrostatic pressure can be applied to alter the lattice parameters. A number of such experiments [21, 22] have found that T_c increases as external pressure is applied, with dT_c/dP increasing as x is decreased, showing increased sensitivity of T_c to x. Similar experiments [2] on $Pr_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ directly correlate with results from internal pressure studies. This sensitive dependence of T_c on pressure is one indicator that the structure has a role [23, 24] in the properties of these materials and that DE is not an adequate theory.

Internal pressure studies show that a decrease in the Mn-O-Mn bond angle arises



Figure 1.3: Phase diagram of temperature versus average A-site size. Open symbols show T_c measured by magnetization and closed symbols are T_c determined by resistivity. Tolerance factor is a measure of the deviation away from perfect cubic structure [2].

from decreasing $\langle r_a \rangle$. The increase in orbital overlap created by pressure allows electrons to delocalize, and the kinetic energy gained by the carriers would seem to be the driving force behind the relationship between $\langle r_a \rangle$ and T_c . In addition, it was found that DE alone cannot give the magnitude of the change in resistivity at T_c [23]. A theory was put forth by Millis [25] which argues that the important parameter governing T_c is the *e-ph* coupling constant λ . Millis' theory is discussed further in Section 1.1.3. The idea that there is a universal relationship between MR and T_c can be seen if we plot T_c for the various phases as a function of x and $\langle r_a \rangle$ as in Figure 1.4. The FM ground state is bound by the size of the La³⁺ ion above and by CO, AF, and spin glass states below which are strongly coupled to lattice



Figure 1.4: Phase diagram of average A-site radius vs. dopant concentration. Effects of Sr and Ca substitution are shown by the dashed lines. Values of T_c are shown in the FMM region[3].

distortions as we might expect since λ is increasingly important in that region.

While the pressure studies attempted to vary only bandwidth or bandfilling, these parameters are too connected to be varied alone. In the $\langle r_a \rangle$ experiments, although x is constant the effective filling likely changes as the *e-ph* coupling is changed. In the external pressure studies, varying the La concentration changes $\langle r_a \rangle$. The *e-ph* coupling, λ , would seem to be the parameter which is actually responsible for the results of these experiments. In Millis' theory [25] an effective λ depends on bandwidth, which in turn depends on the spin alignment through the usual DE expression, and this would seem to fit well with the observed phenomenology.

1.1.3 Experimental evidence for a strong electron lattice interaction

Other experiments have strongly suggested an important interaction between the electron and the lattice. One of these was a study of the isotope effect in La_{0.8}Ca_{0.2}MnO₃ [26]. After a 95 per cent exchange of ¹⁸0 for ¹⁶0, a reduction of T_c from 210K to 190K was observed. No change was seen in SrRuO₃, an itinerant ferromagnet, which had 80 per cent exchange.

A number of other experiments including XAFS [27, 28] and diffraction studies [29] have found large thermal factors on oxygen sites in the PI phase which drop rapidly near T_c . All of these experiments demonstrate that the transition from PI to FM is not solely electronic in origin and that *e-ph* coupling must play an important part. The theory of Millis [25] attempts to explain the electron-lattice interaction in terms of polarons (see Section 1.3.2). Localized carriers in the PI state are believed to distort their immediate environment, and it is this distortion which XAFS and diffraction experiments may be sensing as exaggerated thermal factors. Other, more specialized types of experiments may be better able to detect and characterize these distortions.

1.2 Measuring local structure

1.2.1 Average and local structure

A typical diffraction experiment analyzes the position and intensity of scattered particles in the form of Bragg peaks. These peaks form when the change in the wavevector, \mathbf{Q} , of the scattered particle is a vector of the reciprocal lattice, \mathbf{K} , of the scattering structure. However, this assumes an infinite, perfectly periodic array of atoms. In the case where imperfections exist, we still recover Bragg peaks but their analysis cannot give us the true picture of the structure in question. Since Bragg scattering arisies from perfect periodic arrangements of atoms, it only carries information about the *average* structure. Average in this sense does not carry its usual meaning, but is often used in place of long-range structure.

Any arrangement of atoms which is ordered over long ranges will be discernible through the analysis of Bragg peaks. Short-range structures which are not spatially ordered do not give rise to Bragg peaks but instead produce diffuse scattering. The analysis of diffuse scattering from single crystals to determine local structure has been done for some time but is hampered by the low collection rate and difficulties of sample preparation.

1.2.2 PDF technique

As we discuss in Chapter 2, the atomic pair distribution function (PDF) technique uses powder diffraction data by Fourier transforming the entire pattern: Bragg peaks and diffuse scattering. The result is a real-space radial projection of the atomic pair correlations. Because the entire diffraction pattern is accepted, this function contains information on both the local and average structure. This technique has been applied for some time to the study of liquids and glasses but with modern synchrotrons and neutron sources it has now been extended to crystalline materials [30].

1.2.3 XAFS

Another experimental approach that gives local structural information is XAFS (Xray Absorption Fine Structure). XAFS works by examining changes in the absorption spectrum near the resonant x-ray energy of a particular ion. At the resonance energy an atom of the resonant species absorbs a photon and photoemits an electron. The outgoing electron wave is backscattered by neighboring atoms and interferes with itself. This gives rise to a measurable modulation of the absorption probability at energies above the absorption edge; the so-called extended x-ray absorption fine structure or XAFS. These fluctuations in the absorption cross-section depend sensitively on details of the local atomic structure and it is possible to infer the local structure from them [31, 32]. This has the advantage of chemical-specificity if one desires to know the structure in the region about one particular type of atom. However, the response of the absorption spectra to structure is highly r-dependent, making information beyond the nearest neighbor somewhat problematic. The PDF has the advantage that it can be applied on all length scales.

1.3 Polarons and the Jahn-Teller effect

1.3.1 Jahn-Teller effect

One type of local distortion that is present in these manganites is caused by the Jahn-Teller effect. This is an atomic distortion which certain ions create in order to break the degeneracy of their electron levels [33, 34]. In our case Mn^{3+} , which has 3 *d*-electrons in the t_{2g} state and one in an e_g state, is a Jahn-Teller ion. In the octahedral coordination of Mn^{3+} , the two e_g levels are degenerate if all six oxygen atoms are equidistant from the manganese. By distorting the octahedra, the two e_g states lose their degeneracy and the electron can occupy the lower of them. In Jahn-Teller ions the energy thus gained is greater than the elastic penalty of stretching bonds. In Mn^{3+} ions this leads to an elongation of the octahedron with the $d_{z^2-r^2}$ orbital occupied.

1.3.2 Polarons

The term polaron is used to refer to a large class of quasiparticles in which a localized charge polarizes the background medium where it resides. In Millis' theory of electronphonon coupling the type of polarons created specifically are small lattice polarons. These form when carriers become self-trapped [35]. The condensed charge cloud exerts a force on the previously charge-balanced environment: attracting and repelling the variously charged ions in its vicinity. This "polarizes" the lattice, hence the name. As the local ions adjust to the new situation, the carrier in turn responds to the new potential created by the shifting ions. It is forced to spatially condense further until it is finally contained on a single atomic site. We might expect to see polarons on Mn sites in the PI phase as a distortion in the position of neighboring oxygen sites.

In the case of $La_{1-x}Ca_xMnO_3$, the existence of polarons and the Jahn-Teller effect depends on the behavior of the carriers. The carriers may be fully localized onto discrete manganese sites, or they may be itinerant, with each site sharing them evenly. The ability of manganese to adopt a mixed valence state means that at finite doping levels, when the carriers are localized a fraction of the Mn ions, 1 - x, can still be in the 3+ state and so will still display a Jahn-Teller distortion. This means the remaining Mn ions carry a 4+ charge which would attract the surrounding oxygen ions, contracting those MnO₆ octahdera and creating a polaron. The two distinct charge states create two distinct local structures which we hope to detect. On the other hand, if the carriers are delocalized, all the manganese ions will carry the equivalent charge of 3 + x. In that case all the octahedra will be identical, with neither Jahn-Teller nor polaronic distortions. Thus the presence of these two effects are not only intimately linked to each other, but also tied to the electronic state.



Figure 1.5: Electronic and magnetic phases of $La_{1-x}Ca_xMnO_3$ [4].

1.4 $La_{1-x}Ca_xMnO_3$

1.4.1 Phase diagram

The phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ has been studied by a number of groups [4, 36] and is reproduced in Figure 1.5. At x = 0, the ground state is an antiferromagnetic insulator (AFI) and a ferromagnetic insulator when 0 < x < 0.2. For 0.2 < x < 0.5the ground state is FM with a T_c which can be driven upwards by the application of a magnetic field, hence the CMR effect. For x > 0.5 the ground state is again AFI although there is a well-defined line in the T_c -x plane in this region which defines a charge-ordering (CO) transition seen from TEM [37]. For $x \approx 0.5$ there are three distinct states: COI, FM, and PI. We will discuss this special case further in Chapter 4.

1.4.2 Average structure

The structure of $La_{1-x}Ca_xMnO_3$ was first studied by several groups [38] in the 1950's. They found for the undoped material orthorhombic, rhombohedral, and monoclinic symmetries could all be found depending on the method of preparation. Later, Elemans *et al.* [13] found the compound to be orthorhombic, space group *Pnma*. The average structure shows a large, ordered, Jahn-Teller distortion which disappears with the presence of the dopant.

1.4.3 Properties

At temperatures above T_c , transport is characterized by an activated resistivity, $\rho(T) \propto exp(\Delta \rho/T)$ [9] where $\Delta \rho \approx 2500 - 1000$ K for $La_{1-x}Ca_xMnO_3$, 0.1 < x < 0.6[39]. Thermopower measurements also show semiconductor-like behavior: $S(T) \propto \Delta S/T$, where $\Delta S \approx 120$ K. In simple semiconductor models with a single carrier type $\Delta \rho = \Delta S$, while the experiments show an order of magnitude difference strongly suggesting an additional excitation. A number of papers [40, 41] have demonstrated that these results are consistent with transport via small polarons.

Hall effect measurements done above and below T_c on films of $La_{1-x}Ca_xMnO_3$ with a T_c around 260K show a carrier density $n \approx 1$ hole/Mn site in the FM region, or about three times the Ca concentration [42]. They also find that the mobility is independent of field near T_c for strengths up to several Tesla. This suggests that CMR is due to a field-induced increase in the density of delocalized carriers, and not to a change in the hopping rate as DE holds.

Optical conductivity measurements of a $La_{0.825}Ca_{0.175}MnO_3$ single crystal [43] found a broad peak centered at about 1.4eV. A similar structure was found in thin film Nd_{0.7}Sr_{0.3}MnO₃ [44]. The authors argue that this peak is the result of a charge-

transfer transition from a $Mn^{3+} e_g$ level split by the Jahn- Teller effect to an unoccupied adjacent $Mn^{4+} e_g$ level. One group [45] studied the optical reflectivity of RMO₃ (R = La, Y; M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu) and found a charge gap for most of these compounds but not in LaMnO₃, which has no Mn^{4+} . The presence of the 1eV feature in the doped versions of this compound supports the polaron theory of transport.

1.5 Summary

The phenomenon of colossal magnetoresistance is of great technological and scientific interest. A qualitative understanding of the phenomenology was made possible by the insights of Zener and his Double exchange model which coupled magnetism and charge transport. Two things have happened recently to renew interest in these materials and this phenomenon. First, an extremely large magnetoresistance (socalled colossal magnetoresistance) has been observed in thin-film samples exciting interest in these materials in possible magnetic field sensing applications. Second, it has been shown that DE alone does not explain the magnitudes of the resistivity changes that are observed. As a result, the importance of the electron-lattice coupling through the Jahn-Teller effect has been proposed by Millis, Roder, and others. These theories suggest that the strong e-ph coupling leads to polaronic effects. It is clearly important to verify these proposals to understand better the CMR phenomenon. The local structure is a useful probe to do this because when lattice polarons form they distort the lattice in their vicinity. This has a small effect on the average crystal structure, but is evident in the local structure. A number of techniques can be used to study local structure but in this thesis we have used exclusively the atomic pair distribution function technique. This is described in detail in Chapter 2 and the results are described and summarized in Chapters 3-5.

Chapter 2

The Pair Distribution Function Technique

2.1 Introduction

All information contained in the PDF comes from the scattering of x-rays and neutrons. Each scattering event involves the interaction of a particle with an atomic potential, causing a change in the particle's momentum and, in general, its energy. By measuring the final states of scattered particles one can determine the nature of the potentials they interact with if the incident state is well known.

In our case [46, 47], to measure atomic structure we are interested in elastic scattering, in which the energy of the scattered particle is unchanged. As soon as we have more than one atom acting as a scattering center we create interference among our scattered particles. When we introduce an infinite periodic array of atoms, we arrive at the well known von Laue condition, yielding Bragg peaks wherever the change in wave vector **Q** of the scattered particle is a vector of the reciprocal lattice, **K**. The analysis of Bragg peaks has been a tool for determining crystal structure since 1913, but is limited only to information on the *average* structure. In the case of a perfect crystal this is no drawback since the average and actual structures are identical on all length scales, but in most materials there are important local deviations away

from the average. Because Bragg scattering arises only from long-range periodicity, it cannot tell us anything about such structures.

Fortunately, disorder within a crystal gives rise to diffuse scattering. As the name implies, this scattering has a broad, oscillatory appearance with very low intensity relative to Bragg peaks. In principle, diffuse scattering can be analysed analogous to Bragg peaks to determine the exact nature of the disordered structures. In practice this is extremely difficult, especially in powder diffraction experiments due to intensity problems and unwanted contributions from Bragg peaks. We need not bother with such issues if we accept both diffuse and Bragg scattering.

The total elastic scattering amplitude for a crystal is given by

$$f_{k}(\theta,\phi) = \int e^{-i\mathbf{k}\cdot\mathbf{x}} U(x) \ e^{i\mathbf{k}\cdot\cdot\mathbf{x}} d^{3}x$$
(2.1)

where \mathbf{k} is the wave vector of the incident plane wave, \mathbf{k}' of the scattered wave, and $U(\mathbf{x})$ is the scattering potential from the array of atoms. We can write this potential as the sum of individual atomic potentials located at each point in the array

$$U(\mathbf{x}) = \sum_{i} U_{i}(\mathbf{R}_{i})$$
(2.2)

where $\mathbf{R}_i = \mathbf{x} - \mathbf{x}_i$. Thus

$$f_{k}(\theta,\phi) = \sum_{i} \left(e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}_{i}} \int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_{i}} U_{i}(\mathbf{R}_{i}) \ d^{3}R_{i} \right) .$$
(2.3)

Squaring this amplitude gives the scattering intensity

$$I(\mathbf{Q}) = U^2(\mathbf{Q}) \sum_{ii'} e^{i\mathbf{Q}\cdot\mathbf{R}_{ii'}}, \qquad (2.4)$$

where $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$ and $\mathbf{R}_{ii'}$ is the vector separating the *i*th and *i*th atoms. $U(\mathbf{Q})$ is the Fourier transform of the atomic potential, called the atomic form factor. We have separated $U(\mathbf{Q})$, which depends only on the atomic potentials, from the rest of the expression. The structure function, S(Q), is then

$$S(Q) = \sum_{ii'} e^{i\mathbf{Q}\cdot\mathbf{R}_{ii'}}, \qquad (2.5)$$

which depends solely on the atomic arrangement. An accurate measurement of S(Q) therefore gives important information about the atomic structure.

If we rewrite $e^{i\mathbf{Q}\cdot\mathbf{x}_i}$ as $1/2\pi\int e^{i\mathbf{Q}\cdot\mathbf{x}} \delta(\mathbf{x}-\mathbf{x}_i)dx$, we can express S(Q) as a Fourier transform

$$S(Q) = \frac{1}{2\pi} \int e^{i\mathbf{Q}\cdot\mathbf{x}} \sum_{ii'} \delta(\mathbf{x} - (\mathbf{x}_i - \mathbf{x}_{i'}) d\mathbf{x} . \qquad (2.6)$$

Notice the double summation, indicating it is not the absolute but rather the relative positions of the atoms which determine $S(\mathbf{Q})$. If the structure is isotropic, we can reduce S(Q) to a one-dimensional integral over the radial coordinate r = |x - x'|,

$$S(Q) = 1 + \frac{4\pi}{Q} \int_0^\infty (\rho(r) - \rho_0) r \sin Qr \, dr \,. \qquad (2.7)$$

Inverting the Fourier transform yields $\rho(r)$, the spherically averaged microscopic atomic density:

$$\rho = \rho_0 + \frac{1}{2\pi^2 r} \int_0^\infty Q(S(Q) - 1) \sin Qr \, dQ \,. \tag{2.8}$$

The function $\rho(r) - \rho_0$ is called the pair-distribution-function (PDF) or pair-correlation function denoting its dependance on the relative positions of atomic pairs. Because we have accepted all elastic scattering within the structure function, the PDF contains information on the average structure as well as local distortions. The PDF label is commonly applied to a number of other correlation functions including $G(r) = 4\pi r [\rho - \rho_0]$. This function has among its advantages a statistical uncertainty that is constant in r. Unless otherwise mentioned I will restrict myself to using PDF to mean G(r).

2.2 Data collection

2.2.1 Neutrons

In contrast to x-rays, which scatter from an atom's electron cloud, neutrons interact directly with the nucleus. The elementary theory of neutron scattering [48, 49] is based on the Born approximation and uses the Fermi pseudopotential to represent the effective interaction between neutrons and nuclei. Because the range of the strong force is much less than the wavelength of thermal neutrons, neutron-nucleus scattering is isotropic, i.e. it contains only s-wave components. It can therefore be characterized by a single parameter, b, the scattering length.

Within the Born approximation, the only potential which gives purely s-wave scattering is a delta function [50]. Using perturbation theory in this case is strictly incorrect because the interaction is very strong, although it is short-ranged. The Fermi psuedopotential merely gives the answer we know to be correct for s-wave scattering. For an array of nuclei this gives a potential with the form

$$V(r) = \frac{2\pi\hbar^2}{m} \sum_{i} b_i \,\delta(\mathbf{r} - \mathbf{R}_i) \,. \tag{2.9}$$

Substituting this potential into Equation 2.1 we obtain

$$f_{k}(\theta,\phi) = \sum_{i} b_{i} \int e^{-i\mathbf{k}'\cdot\mathbf{r}} \,\delta(\mathbf{r}-\mathbf{R}_{i}) \,e^{i\mathbf{k}\cdot\mathbf{r}} \,d\mathbf{r} \,. \tag{2.10}$$

As in Equation 2.4, we can separate $U(\mathbf{Q})$, the Fourier transform of the potential, from the rest of the expression for the scattered intensity. Because the atomic potential is a delta function, its Fourier transform is merely the scalar constant b. This is much , simpler than the atomic form factor for x-rays, removing one level of difficulty in obtaining $S(\mathbf{Q})$ from the measured intensity.

All the neutron diffraction measurements described herein were performed at the Special Environment Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) and the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan Jr. Neutron Science Center (MLNSC) at Los Alamos National Laboratory. In both cases, pulses of neutrons are produced by accelerating bundles of protons into a heavy metal target. For example, at IPNS the protons achieve 450MeV and strike the target at a frequency of 30Hz. The resulting spallation produces a pulse of neutrons which enter a moderator of liquid methane kept at 100K. The moderator produces a spectrum of neutrons with wavelengths from ≈ 0.25 Å to 8Å, suitable for elastic scattering. At the SEPD, the pulse travels down an evacuated flight path of 14 meters before striking the sample, which is a fine powder sealed in a hollow vanadium tube about 2 inches tall and 1/4 inch in diameter. Since the MLNSC operates on similar principles, I will only refer to it where there are significant differences. The vanadium can is mounted onto a displex, helium refrigerator. The sample temperature can be controlled to within $\approx 2/10$ of a degree from 8K to 300K. A Helium atmosphere is maintained within the vanadium can to act as an exchange gas and ensure good thermal contact between the cold stage and the sample.

After being scattered by the sample, the neutrons travel to a surrounding array of detectors 1.5 meters away. The time of arrival as well as the location of incoming neutrons is recorded in order to determine the momentum transfer, Q. In the case of elastic scattering, $Q = 4\pi \sin(\theta/\lambda)$ where λ is the wavelength of the neutron and θ is half the scattering angle. Knowing the time of a neutron's arrival allows us to determine the wavelength from the total time of flight since all the particles emerge from the target together in a pulse. The total time of flight t = L/v where L is the total flight length and v is the speed. Knowing v we have the magnitude of the momentum, and the deBroglie relation gives us the wavelength, $\lambda = h/p$. Since each detector is at a fixed position, we also know the scattering angle for each detected particle.

There are 130 total detectors, located in ten individual banks. These banks are time focused onto nominal 2θ angles of \pm 15, 30, 60, 90 and 150°. Time focusing is a process whereby arrival times at a detector located at $2\theta + \delta\theta$ are modified to give them the times they would have had at 2θ . This maps data from multiple detectors onto a single effective detector without significant loss of resolution. The data at positive and negative angles are summed together, leaving only five separate banks. Because of the finite neutron spectrum and the different locations of the detectors, each bank covers a different range of Q and has a different resolution. We will see in the next section that Q resolution is rarely an issue in obtaining accurate PDFs, so all the banks are summed together to cover the greatest range of Q possible with the best statistics. For manganites, four to six hours usually provides adequate counts to obtain highly reproducible PDFs.

In order to remove scattering which does not come from the sample, additional data must be taken to characterize the experimental conditions. A background run is taken, which includes scattering from the displex and heat shields. Also, a run is taken to measure the scattering from the empty sample container. And finally, a vanadium rod is used as a reference sample to characterize the detector efficiency and source spectrum. The procedure for applying these data to correct S(Q) will be discussed in the Analysis section.



Figure 2.1: X-ray parafocusing geometry. The detector and the source are kept equidistant from the sample.

2.2.2 X-Rays

Although the underlying scattering mechanism is different, elastic x-ray scattering can also be used to obtain a structure function and a PDF. Unfortunately, we cannot blast a sample with a broad spectrum of x-rays and obtain useful information because we cannot recover Q through time of flight measurements as with neutrons. Energy-dispersive x-ray measurements are possible with a polychromatic source and an energy-sensitive detector. However it is much simpler to use the angle-dispersive method, in which a single wavelength is chosen and the scattering angle is systematically rotated.

Our x-ray experiments are performed on a Huber four-circle diffractometer. Xrays are produced from a sealed tube with a silver cathode kept at 45kV. A graphite monochromator is used to select the K α_1 emission, with a wavelength of 0.559Å. Two sets of slits define the beam on the sample, a fine powder mounted onto a flat plate. The plate is centered on a circle which rotates, defining θ . A scintillation-counter is mounted on a circle which rotates at twice the rate of the sample to maintain the detector at 2θ . With the source-to-sample distance equal to the sample-to-detector distance, this arrangement generates 'parafocusing', shown in Fig. 2.1 This allows us to use a divergent beam, thus better counting statistics, and still maintain reasonable resoultion.

Data are collected incrementally, one Q-value at a time, with θ and 2θ systematically rotated over the entire accessible range. With Ag K α_1 radiation we can reach a maximum Q of $\approx 21 \text{\AA}^{-1}$. Low count rates, particularly at high 2θ , can stretch collection times to several days. This can vary greatly depending on the scattering power of the sample. Each element has a well-defined scattering length b_i , which is used to define its scattering cross section $\sigma_i = 4\pi b_i^2$. X-ray scattering lengths are proportional to the number of electrons an atom contains. Thus, a sample made from heavy elements will scatter strongly. Unfortunately, the oxygen in La_{1-x}Ca_xMnO₃ makes it only a weak xray scatterer.

The sample environment is again a helium displex, used to maintain a steady temperature down to ≈ 10 K. X-rays penetrate through a Berrylium window in the vacuum shroud. Low-Z elements such as Berrylium are virtually transparent to x-rays, and the window does not contribute to the scattering in any noticeable way. The geometry of the displex makes it impossible to measure the background directly, so the beam is carefully focused to avoid scattering off the sample holder. In addition, the sample can be held in place by mixing it with a polymer that produces very little signal.

Because of the intrinsically low intensity of the x-ray source it is of paramount importance to ensure proper alignment of the diffractometer. This begins with setting the monochromator correctly to select the desired wavelength. The sample must be in the physical center of the theta circle so that it does not translate when rotated. The beam must strike the sample squarely and all slits must be in a position to allow a minimum of background scattering while preserving maximum scattered intensity.

2.3 Analysis

In an ideal case, a PDF would be calculated from a structure function which depends only on the structure of the sample. Experimentally, we can never eliminate contributions from extraneous sources which contaminate the measured S(Q). A series of corrections are necessary to recover only the scattering which arises from the sample.

2.3.1 Neutrons

The characterization scans described in the last section are designed to allow the structure function to be recovered from real data as accurately as possible. First, the instrument background intensity is removed. A constant background of delayed neutrons must also be subtracted. These neutrons emerge from the source with the same energy spectrum as the pulse but at a different time, making time-of-flight calculations impossible. Since they account for a background of approximately 3-5 per cent of the scattered flux they can easily be accounted for.

Next we must account for neutrons which are inelastically scattered. Since the detectors only measure the time of flight, and not the actual energy of a neutron, the Q-bin which an inelastically scattered neutron is placed in will be incorrect. The shift in Q is due to the neutron being slowed or accelerated in the scattering process.

The amount of inelastic scattering at low Q is a tiny fraction of the elastic scattering, but as Q rises it quickly becomes significant. When $Q > 3\sigma_{DW}$ the inelastic scattering dominates the diffraction pattern, where σ_{DW} is the Debye-Waller temperature factor. This is the width of the Gaussian envelope which damps the intensity of Bragg peaks as a function of Q due to the uncorrelated motion of the atoms. The error in Q-binning still should not produce a large effect because features in inelastic scattering such as phonon dispersions tend to be broad and vary slowly with Q. In addition, assuming we understand the sources of the inelastic scattering, we can rebin a predicted quantity of neutrons into their correct Q-values. This is known as a Placzek correction and is discussed by a number of authors [51, 52].

Corrections for absorption and multiple scattering are calculated for cylindrical samples following the procedure of Price [53] and Blech and Averbach [54]. This takes into account the absorption and multiple scattering from the sample as well as the container, and corrects these effects before the container scattering is subtracted from the total. Finally, the source spectrum and detector efficiency are accounted for. This is done by taking the ratio of structure factors from the sample to structure factors from a reference vanadium rod. Vanadium is an almost perfectly incoherent scatterer of neutrons and so the scattering intensity measured from a vanadium rod reflects the incident spectrum modified by the detector efficiency.

Before calculating the PDF, we convert S(Q) into the single-particle structure function by dividing by the total number of scatterers. This should yield a normalized function which goes to 1 as Q approaches infinity. In practice, the density of the sample during the experiment and the volume irradiated by the beam are not precisely known so the effective density is varied as a parameter until the proper normalization condition is met.

2.3.2 X-Rays

Extracting a PDF from x-ray data uses the same fundamental mathematics, but some different corrections must be made. In our case, no sample holder or shielding is in the path of the beam so no characterization runs are needed as with neutron data. Because x-rays are scattered off electrons, the finite size of the atom must be taken into account. This is done by dividing the scattered intensity by the average form factor, which contains the Q-dependence of the scattering due to the atom's physical


Figure 2.2: Structure function of $La_{1-x}Ca_xMnO_3$ up to 22\AA^{-1} .

extent. As neutrons scatter off of the atomic nucleus, we can ignore the neutron form factor.

Compton scattering is another challenge posed by x-rays. While Compton-scattered photons should always have a lower energy than elastic scattering, it is difficult to discriminate between them, especially at low angles. Therefore, both Compton and elastic scattering is accepted. The contribution due to Compton is calculated from theory and subtracted from the data. Absorption and multiple scattering are removed similarly as in the case of neutrons. After these corrections are applied, the resulting structure function can be processed to obtain a PDF without regard to the method of data collection. Figure 2.2 shows a typical structure function from $La_{1-x}Ca_xMnO_3$.



Figure 2.3: Typical neutron PDF of $La_{1-x}Ca_xMnO_3$.

2.3.3 Obtaining the PDF

After S(Q) is known, the PDF is calculated through direct Fourier transform, according to Equation 2.8. Figure 2.3 shows a PDF calculated from the structure function in Figure 2.2. Care must be used in determining the range of Q to keep when carrying out the integral. Going to higher Q improves the resolution of the PDF, but the count rate tends to fall quickly with rising Q. Thus, we Fourier transform a higher fraction of noise as we increase Q_{max} and the benefit of improved resolution is washed out by increasing statistical fluctuations.

Fourier transforming the structure function with its finite Q-range will introduce high-frequency termination ripples into the PDF, which will be discussed in the next section. These arise from the convolution of S(Q) with a step function. Applying a damping function to high-Q data so that S(Q) smoothly approaches 1 at high Q is a common practice but its benefits are mainly cosmetic. It does reduce termination ripples but at the cost of broadening PDF peaks due to the loss of high-Q information. The same can be achieved by simply choosing a lower Q_{max} . Since the termination ripples produced by the convolution can be mimicked in the modeling stage, we have not used any damping.

2.4 Modeling

Although modeling is an important element in determining local structural information from PDFs, most of this work will not refer to results obtained from any modeling. Therefore, I will only briefly discuss the features of the procedure. In general, the average structure of a material is known from a Rietveld refinement of powder diffraction data or some other means. These parameters, including atomic positions, thermal factors, and occupancies, can be taken as a starting point to calculate a model-PDF. Parameters may be refined using a least-squares fitting routine while preserving the long-range order of the system. The agreement of this model-PDF with data tells us how well the long-range ordered structure does at fitting the local structure.

Once the best fit has been achieved using the constraints of the average structure, local distortions and/or occupancy inhomogeneities may be introduced into the local structure. Once again these variables may be refined to look for a local structure which is superior to the average. Clearly the parameter space can be enormous so unless there is some indication of the type of distortion necessary to fit the data it can be very difficult to identify through modeling.

2.5 PDF peak height and width

A simple yet important way to learn about disorder from a PDF without resorting to modeling is to examine the height and width of PDF peaks. Each peak in the PDF arises from a pair of atoms separated by a particular distance. A perfect experiment on a fully-ordered crystal with static atoms would yield a series of delta functions, located at every r-value which separates an atomic pair. Actual peaks have a finite width because of the intrinsic thermal and static disorder within a solid, as well as convolution effects. However, the integrated area of a given peak must be conserved since that depends on the total number of contributing atoms. Therefore, any change in the height, and therefore width, of a peak means a change in the disorder associated with that particular correlation since we always convolute our structure functions identically. If we have a number of PDFs, measured at closely spaced values of temperature or composition, we can compare heights of various peaks to spot when local disorder increases or decreases and which atoms are affected. While this alone cannot tell us the shape of distortions, it does tell us when external parameters are having an impact on local structure.

Chapter 3

Metal-Insulator Transition at T_c and x_c

3.1 Introduction

In this research we use the local atomic structure as a probe of the electronic state of the CMR materials from the system $La_{1-x}Ca_xMnO_3$. In particular we are interested in determining whether local Jahn-Teller distorted octahedra can be detected, whether polaronic distortions can be detected and characterized, and whether these features have a temperature or composition dependence. As we will see, these features can be seen and have a particularly large response to the metal-insulator transition. In this chapter we describe the nature of the JT and polaronic distortions and how they change on crossing the metal-insulator transition as a function of temperature. We will also describe preliminary results of what happens as the MI transition at $\sim x = 0.18$ is crossed at low-temperature as a function of doping. In the next chapter we will look at the temperature dependence of a sample with x = 0.5 which lies exactly on another low-T MI-transition. Finally, in Chapter 5, we sum up.

3.2 Structural Response to Temperature

To look for the signs of lattice polarons at T_c we performed neutron diffraction on $La_{1-x}Ca_xMnO_3$ samples with x = 0.12, 0.21, and 0.25 at temperatures ranging from 10-300K looking for changes in the PDF corresponding with the MI transition. Samples were made by Dr. J. J. Neumeier at Los Alamos National Lab (LANL) by a solid state reaction of La_2CO_3 , $CaCO_3$ and MnO_2 with repeated grindings and firings at temperatures up to 1400°C, with a final slow cool at 1°C per minute. The nominal Mn valences were determined by idometric titration and were 3.25, 3.24, and 3.29 for the x = 0.12, 0.21, and 0.25, respectively. The DC magnetization was measured at LANL using a commercial SQUID magnetometer and the temperature dependent resistivity was measured using the standard 4-probe dc technique. Neutron data were collected at the Special Environment Powder Diffractometer (SEPD) instrument at the Intense Pulsed Neutron Source (IPNS) and at the Manuel Lujan Jr. Neutron Scattering Center (MLNSC) at Los Alamos National Laboratory. Collection and Analysis procedures are described in Chapter 2.

Figure 3.1 shows PDFs obtained from $La_{0.88}Ca_{0.12}MnO_3$ at 150K and 180K. This sample has no MI transition, hence we only expect the structure to change slightly due to thermal effects. The difference in PDFs is plotted below the data and shows reproducibility within statistical uncertainty. Compare this with Figure 3.2, which shows PDFs of $La_{0.79}Ca_{0.21}MnO_3$ at 160K and 192K. This sample has a MI transition, at approximately 182K. We see that the PDFs match up substantially less well, particularly in the region of the first two peaks at the low-*r* end of the PDF.

Table 3.1 shows all the atomic pair correlations below 2.75Å, and their respective amplitudes based on the crystal structure. Note that the first PDF peak in $La_{1-x}Ca_xMnO_3$ arises from correlations between Mn and neighboring oxygen atoms.



Figure 3.1: PDFs of $La_{0.88}Ca_{0.12}MnO_3$ measured at 150K and 188K, difference plotted below. Dashed lines indicate two-sigma level of uncertainty. Note that the difference curve remains largely within the dashed lines, showing that the structure remains largely unchanged.

Any changes in the size or shape of the MnO_6 octahedra will be reflected in changes of this peak. The second peak at r = 2.75Å is largely due to neighboring oxygen-oxygen correlations, although there are also contributions from La/Ca-oxygen and La/Ca-La/Ca pairs. These two peaks, and no others, are directly dependent on the structure of the MnO_6 octahedra. The appearance of changes in the PDF at these peaks is suggestive of polaron formation, which would distort the local arrangement of oxygen atoms. In order to confirm this, we fit models containing polaronic distortions to the data and compared the results to fits containing no distortions. Unfortunately, the structural differences proved too small for our fitting program to distinguish between. We therefore resorted to examining peak-heights.



Figure 3.2: PDFs of $La_{0.88}Ca_{0.12}MnO_3$ measured at 160K and 192K, difference plotted below. Note the large amplitude of the difference curve relative to the uncertainty. Between these temperatures the sample has passed through the MI transition and the structure has changed noticeably.

3.2.1 Atomic disorder from PDF peak-heights

In Chapter 2 we mentioned that the sharpness of an individual PDF peak is determined by (among other things) the degree of static and/or dynamic disorder present in the contributing correlations. In the case of a temperature-dependent study, as T increases peaks should become broader due to increased thermal vibration. Since the integrated intensity under each peak must remain constant, the height of that peak must decrease. The same holds true in the case of static disorder: an increase will cause associated peaks to broaden and lose height. In $La_{1-x}Ca_xMnO_3$ we are interested in polaronic and Jahn-Teller distortions which should impact short-range Mn-oxygen and oxygen-oxygen correlations. Since individual PDFs show changes in

Table 3.1: First seventeen atomic correlations and amplitudes for $La_{1-x}Ca_xMnO_3$ based on the crystal structure model. Note the strong Mn-O peak at 1.96Å and the strong O-O peak at 2.74Å.

Atom 1	Atom 2	r (Angst)	amplitude
Mn	01	1.9600	0.8000
Mn	O2	1.9600	0.4000
Ca	O2	2.4200	0.0250
La	O2	2.4200	0.0750
Ca	O2	2.4300	0.0250
La	O2	2.4300	0.0750
Ca	01	2.4700	0.1000
La	01	2.4700	0.3000
Ca	O2	2.6000	0.0250
La	O2	2.6000	0.0750
Ca	01	2.6400	0.1000
La	01	2.6400	0.3000
Ca	O2	2.6900	0.0250
La	O2	2.6900	0.0750
01	O2	2.7300	0.2000
01	01	2.7400	0.8000
01	O2	2.7400	0.2000

the corresponding low-r peaks, we plot the height of these peaks as a function of temperature.

Figure 3.3 shows the height of the r = 2.75Å peak as a function of temperature for three different samples. Both this and the 1.9Å peak show the same qualitative behavior. We concentrate on the r = 2.75Å, however, because the statistical and systematic errors on this peak are smaller. The reason for the former is that the peak is much stronger (there are 12 O-O bonds contributing to this peak instead of just 6 M-O bonds for the 1.9Å peak) and for the latter we note that systematic errors tend to die out with increasing-r in the PDF since they tend to originate from longwavelength artifacts in S(Q) coming from inadequate data corrections. Beginning with the bottom panel, peak-heights for the x = 0.12 sample drop smoothly with



Figure 3.3: Peak heights vs. temperature for three compositions: x = 0.25 (top), x = 0.21 (middle), and x = 0.12 (bottom). The upper two panels show a large drop in height well below T_c , marked with arrow. Bottom panel shows a composition with no MI transition. The peak heights follow the expected Debye behavior. Insets show resistivity vs. temperature.

increased temperature. The solid line is a prediction of expected thermal broadening, calculated using the Debye model [47, 55]. Again, this sample has no MI transition and we see that the drop in peak-height is well fit by thermal motion.

The middle panel shows the data from the x = 0.21 sample. The same Debye curve is plotted, and the data in this and the bottom panel have been re-scaled so that the low-temperature points lie near the curve. As T_c is approached there is a very large drop in peak-height which begins at least forty degrees below T_c and continues right up to and perhaps a bit beyond the transition temperature. A similar large effect is seen in the x = 0.25 sample in the top panel. This sudden drop in height is not explained by thermal effects and must be due to a sudden increase in structural disorder of the MnO₆ octahedra. Such a change, taking place at the temperatures where the sample is leaving the metallic phase, is just what one might expect if the mechanism becomes polaronic at high-T. In Section 3.4 we will discuss our efforts to characterize the size and shape of these polarons.

3.3 Doping across the phase transition

We can only conclude from the previous section that the local structure becomes more disordered above T_c and that it is relatively more ordered below. We have not shown that the metallic phase is free from polaronic or Jahn-Teller effects, merely that such distortions seem to increase upon approach of the insulating state. In order to determine this, and to help establish that the PI state is indeed polaronic, we examine local structural changes as a function of composition.

Once again we carried out neutron diffraction over a range of temperatures on samples with doping values of x = 0.21 and x = 0.12. Figure 3.4 shows PDFs for each sample measured at 10K in the lower panel. Clearly, there are significant differences between the two structures. This in itself is not surprising as the two are chemically distinct materials as well as being in different phases: the lower-doped sample has no metallic state and is a ferromagnetic insulator at low temperatures. The upper panel shows PDFs for the same two samples measured at 220K. Here the x = 0.21 sample has passed through T_c and is fully in the insulating phase. Now the two structures are virtually indistinguishable. The compositional differences therefore



Figure 3.4: PDFs of La_{0.79}Ca_{0.21}MnO₃ and La_{0.88}Ca_{0.12}MnO₃. (A) Both measured at 220K, both in the insulating phase. The structures are remarkably similar although the compositions are different.(B) Both measured at 10K, the x = 0.21 sample is now in the FM phase and is sharper relative to the x = 0.12 sample.

do not appear to impact the PDFs significantly, while crossing the MI transition line seems to make both samples structurally identical. This can be explained if small polarons, present in the respective insulating phases, disappear when entering the metallic regime regardless of whether they do so because of a decrease in temperature or an increase in doping.

We can test whether this is so by examining changes in the PDFs as a function of temperature and composition. Figure 3.5 shows a pair of PDF difference curves. The solid line is the difference between x = 0.12 and x = 0.21 samples at 220K



Figure 3.5: Comparison of PDF difference curves between $La_{0.79}Ca_{0.21}MnO_3$ and $La_{0.88}Ca_{0.12}MnO_3$ at 220K (solid line) and 10K (triangles). At low temperature, when the two samples are in different phases, the structures show larger differences than at higher temperatures at which they are both PI.

and the triangles are the differences between the PDFs at 10K from Figure 3.4. We see again that the changes at low temperature are much greater, and there appears to be no significant correlation between the two curves. Thus we can reasonably rule out chemical differences as a major source of structural changes between these two samples. However, if we again plot the difference curve at 10K in Figure 3.6, together with the difference between x = 0.21 sample at 225K and 140K, we see a remarkable coincidence. Once again, the solid line in Figure 3.6 is the difference caused by a decrease in temperature through the insulator-metal transition of the higher-doped sample while the triangles show the difference when doping is increased through the insulator-metal transition at low temperature. There is no reason for these



Figure 3.6: Difference curves: Triangles are again the difference between $La_{0.79}Ca_{0.21}MnO_3$ and $La_{0.88}Ca_{0.12}MnO_3$ PDFs at 10K. Solid line is the difference between $La_{0.79}Ca_{0.21}MnO_3$ at 225K and 140K. The changes in the structure caused by entering the FM phase through a decrease in temperature or an increase in doping are large and correlate well.

two changes to have similar effects on a structure, yet we see that both curves are large and strongly correlated over a wide range of r. The only thing these difference curves have in common is they were both produced by crossing from the insulating to the metallic phase, albeit via different paths.

These results point out that in this compositional region, the division of the phase diagram between metallic and insulating phases also separates two distinct local structures. The insulating phase is identified by local distortions caused by polarons which are not seen in the metallic phase.

3.3.1 Within the metallic region

In the previous discussion we considered only compositions which lie well inside their respective phases. This does not address how the system evolves from one state to another: whether it changes suddenly or continuously passes through a series of intermediate structures from disordered to fully ordered. Distinguishing between these two modes of behavior is important because this will tell a great deal about the electronic state of both the metallic and insulating regions.

If the structure gradually becomes more ordered as we increase doping at low temperature across the phase boundary into the metallic region, then the two phases are qualitatively similar on a microscopic scale. They both contain a mixture of distorted and undistorted MnO_6 octahedra with a ratio set by the doping level. The structure becomes more ordered with increased doping because the number of Jahn-Teller distorted sites drops proportionally. In this case the metallic state is not created by any change in the behavior of carriers but merely by changing the relative number of holes and electrons. This would support a percolative model [56, 57] for the phase transition whereby transport is enhanced once a contiguous path of Mn^{4+} is established. In this case polarons would still exist in at least some of the metallic phase, albeit in smaller numbers.

On the other hand, if the structure remains relatively unchanged below the critical doping value and then suddenly becomes ordered upon crossing the phase boundary, this would indicate a qualitative difference in the nature of the carriers in the two phases. The discontinuous increase in structural order could be explained by a delocalization of carriers, creating a uniform distribution of non-Jahn-Teller distorted octahedra. Therefore, determining the structure will tell us a great deal about the mechanism responsible for the change in electromagnetic properties.



Figure 3.7: Height of the Mn-O peak at 10K vs. Calcium concentration. Dashed line shows the boundary composition between insulating and metallic regions at this temperature. The peak sharpens smoothly through x_{MI} and continues sharpening well into the FM phase. This suggests that local distortions exist close to the phase boundary even at low temperatures.

Figure 3.7 shows the height of the Mn-O peak taken from PDFs of 14 samples at 10K with compositions ranging from x = 0 to x = 0.4, concentrated about the critical doping value of 0.19. With the exception of the x = 0 sample, all the data were collected on the same device during one continuous run under identical conditions to maximize reproducibility. Clearly the structure is undergoing a transition over a wide span of composition from most disordered at x = 0 until saturation at about x = 0.22. This would strongly support the percolation argument for metallicity as we see no discontinuity at the phase transformation as well as some persistent disorder in the metallic regime. Unfortunately, susceptibility measurements showed high degrees of inhomogeneity in the higher-doped samples which would smear out the MI transition's position even if it were occuring at a single value. The samples with lower doping levels were closer to an ideal homogeneous state, and the linear behavior of their peak-heights makes it tempting to say we are seeing a linear evolution toward the ordered state but until adequate samples can be re-tested the result is inconclusive. This requires considerable beam-time and has not been carried out to date.

3.4 Polarons and modeling

3.4.1 Fitting the Jahn-Teller distortion

Beyond simply measuring changes in peak-height to look for local distortions, we can learn something about the nature of the MnO₆ octahedra through modeling. Looking at Figure 3.2 we immediately notice a difference between PDFs of manganites in the metallic and insulating phases. The first peak in the metallic phase, besides being sharper as we discussed previously, has a noticeable secondary peak appearing as a shoulder near 2.2Å which is conspicuously absent when the same material is in the insulating phase. This qualitative difference is repeated over the entire doping range 0 < x < 0.5.

At first glance, this secondary peak would seem to present a contradiction. If we presume that the metallic state is more ordered, with polaronic and Jahn-Teller distortions appearing as the insulating state is approached, we might hope to see secondary Mn-O peaks in that region arising from the inhomogeneous distribution of Mn-O bond-lengths. Instead, the reverse is true. One could argue that this secondary peak is evidence of a local, full magnitude Jahn-Teller distortion within the metallic region at *all* temperatures. While we would agree there are residual distortions in the metallic region near the phase boundary, we shall see that this secondary peak is an experimental artifact.

In Chapter 2 we discussed the effects of convolution in the Fourier integral due to finite data in Q-space. As we know, convolution with a step function will cause sharp peaks in the PDF to broaden, as well as introducing ripples according to the



Figure 3.8: Undistorted crystal model fit to $La_{0.75}Ca_{0.25}MnO_3$ in the FM phase at 20K (left) and in the PI phase at 260K (right). Darker lines are data. Note that the quality of the fit is considerably poorer at the higher temperature.

equation [58]

$$G_e(r) = \frac{1}{\pi} \int_0^\infty G(r') \left[\frac{\sin q_{max}(r-r')}{r-r'} - \frac{\sin q_{max}(r+r')}{r+r'} \right] dr'$$
(3.1)

where G(r) is the theoretically calculated function and $G_e(r)$ is that function measured experimentally. Of course, we can convolute any model we wish to calculate in the same manner. A model based on an undistorted crystal structure, i.e. a single Mn-O bond-length, is plotted in the left panel of Figure 3.8 together with a PDF from La_{0.75}Ca_{0.25}MnO₃ measured at 20K.

The data had a Q-max of 22\AA^{-1} so the model was convoluted with the corresponding step function to reproduce the broadening and ripple pattern. Notice that both the 1.9Å peak as well as the secondary peak at 2.3Å are reproduced by the model. This model has no correlations at 2.3Å, the existence of a peak in the model PDF is due to the sharpness of the 1.9Å peak in the metallic phase. Since the structure is well-ordered in this region, and the motion of neighboring atoms is highly correlated,

this peak should have the smallest natural width in the entire PDF, hence it will show the greatest effects of the convolution. In contrast, the right panel in Figure 3.8 shows a PDF from $La_{0.75}Ca_{0.25}MnO_3$ at 250K together with a fit from the same undistorted model. Notice that the model once again has a peak at 2.3Å which fails to fit the data at all. Because the 1.9Å peak is so broadened by distortions in the PI phase, clearly visible in its decreased height, the effects of convolution on its appearance are greatly diminished. The model, which assumes no distortions, still preserves the secondary feature. However, the data shows a great deal of intensity in the region between the two peaks which the model completely misses. This feature is in the wrong position and has the wrong shape to be a termination ripple, it can only be intensity which has escaped from the first peak. It is this feature, and not the 2.3Å peak, which is the signature of a long Mn-O bond caused by Jahn-Teller distortions. The extremely good fit of the undistorted model to the data in the metallic phase convinces us that at very low temperatures well inside the FM state, the structure is free from local distortions. However, as we have seen the height of the low-r peaks begin to fall well below T_c and this model gradually fails to capture the correct low-r features as temperature increases within the FM region. This indicates that there are distortions present within much of the FM phase arising from a coexistence of delocalized carriers and polarons. In Chapter Four we will see this situation arise again.

Chapter 4

Metal Insulator Transition at x=0.5

4.1 Introduction

In $\operatorname{La}_{1-x}\operatorname{Ca}_x\operatorname{MnO}_3$ there is a MI transition at low temperature on increasing Ca content through x = 0.5 [4, 59]. The MI boundary is almost vertical on the x vs. T phase diagram. The composition $\operatorname{La}_{1-x}\operatorname{Ca}_x\operatorname{MnO}_3$ with x = 0.5 is clearly a very special material which has marginal properties and which can hardly decide between having a ferromagnetic metallic groundstate (characteristic of x < 0.5) or an antiferromagnetic, charge-ordered, insulating ground-state (characteristic of x > 0.5). In fact, on cooling the sample goes from a paramagnetic insulator at high temperature first to a ferromagnet with improved metallic properties. On further cooling it charge-orders with an incommensurate ordering vector. Finally, at low temperature, the spins order antiferromagnetically. The sample has the charge-ordered insulating ground-state, but only marginally.

The interesting possibility exists that on cooling the charges delocalize, the small polarons evident at high-temperature are destroyed, but on further cooling they reform in an ordered array at low-temperature. An alternative possibility is that the polarons exist at all temperatures and on charge-melting they undergo an orderdisorder transition. In this picture, it is not clear what gives rise to the ferromagnetic phase at intermediate temperature. Clearly, the PDF is a useful tool for diagnosing the local state of the carriers in the intermediate phases.

The evolution of the phases in the x = 0.5 sample is as follows. The ground state is antiferromagnetic and charge ordered in striped arrays [60] until ≈ 155 K where there is a transition to a ferromagnetic metallic (FM) state. This region is considered more metallic only in the sense that the reisitivity curve bends downwards. Initially, charge ordering survives in the FM state but it gradually becomes more incommensurate with temperature [61]. At ≈ 225 K a second transition results in a paramagnetic insulating (PI) phase with activated polaronic transport [4]. The existence of all three distinct phases, specific to this particular composition, allows one to study two separate MI transitions within the same sample. Thus we can determine if the polaronic distortions seen in the low-temperature insulating phase reappear after crossing the intermediate metallic state.

4.2 Experiments and results

Measurements were made during both cooling and warming cycles, ranging between 15K and 325K using a closed cycle helium refrigerator. Examples of G(r) are shown in Figure 4.1.

Two sets of data are plotted together to demonstrate the level of reproducibility. They were both measured at 112K, well into the charge ordered phase, first upon cooling and then while warming. The difference curve, plotted below the data, is seen to fall largely within the dashed lines, which show uncertainties due to statistical fluctuations at the level of two standard deviations. Thus we conclude that PDFs obtained as a function of temperature are reproducible within the limits of statistical



Figure 4.1: PDFs of $La_{0.50}Ca_{0.50}MnO_3$ measured at 112K. The solid line is the PDF measure while warming and the circles while cooling. Difference is plotted underneath. Dashed lines indicate two sigmas of statistical uncertainty. Note the close agreement between PDFs.

noise.

We begin looking for structural changes by examining PDF peak-heights as a function of temperature. As discussed, peak-height is a strong indicator of changes in the degree of structural disorder within a given correlation. If there were a sudden increase in the disorder of the arrangement of atoms which contribute to a given correlation, that peak would broaden and its height would show a correspondingly sudden decrease. This would be directly analogous to a sharp *increase* in refined thermal parameters.

The top panel of Figure 4.2 shows the height of a peak at 16.2Å as a function of temperature. The peak's height clearly drops once the sample enters the charge ordered region. This behavior is reproduced in a number of other peaks located at



Figure 4.2: Top: Heights of PDF peak at 16.2Å as a function of temperature. Squares indicate data collected while warming, circles while cooling. Peak height rises dramatically with temperature between T_N and T_{CO} . This is due to the loss of charge ordering which leads to a higher symmetry state. Bottom: Heights of PDF peak at 2.75Å. Peak heights tend to follow Debye curve (solid line) except on cooling between T_c and T_N . Those peak heights (filled circles) increase due to charge delocalization which is suppressed by charge-ordering.

higher $(>10\text{\AA})$ values of r. This indicates some change of the average structure into a higher symmetry state because peak-heights are increasing as the temperature rises. This is more remarkable considering that thermal effects are simultaneously broadening these peaks. However, on shorter length scales the structure evolves differently over the same temperature range.

The strong positive peak in the PDF at $r \approx 2.75$ Å arises primarily from oxygenoxygen correlations and so is a good indicator of changes in the shape of the oxygen octahedra which surround the manganese ions. The bottom panel in Figure 4.2 shows the height of this peak: the large changes seen on intermediate length scales are gone. The first PDF peak, at 1.9Å, shows the same qualitative behavior. This peak arises solely from Mn-O correlations and so is also sensitive to local distortions of the octahedra. As the carriers clearly are localized in the charge ordered state, this suggests that they remain so throughout this entire temperature range, because we can observe a large effect that delocalization has on this peak [47]. Therefore, while charge ordering gradually disappears in the FM state, localized charges persist but the charge ordering melts away through an order-disorder transition.

If we again examine the bottom panel of Figure 4.2 we notice interesting behavior in the FM state. The solid line shows shows the change in peak-height expected due to thermal motion predicted by the Debye law. Most of the points lie on or near this line, and the cooling and warming cycles show good agreement except in the hysteretic region. This indicates that there is some response of the Mn-O₆ octahedron to the electronic and magnetic transitions, but certainly a subtler one than that seen on longer length scales. In particular, the cooling cycle points between T_{fm} (shown by the dashed line) and T_{co} are shifted up away from the Debye curve even though the 16.2Å peak shows no change at this point and there are no charge ordering superlattice peaks. The octahedra are responding to the increase in metallicity. We do not see a similar effect on the warming cycle because there is no temperature range in that case where the sample is ferromagnetic without being charge ordered also.

We can compare the sharpening of this peak to that observed in lower doped samples. In this material the sharpening is much less than that seen in the x = 0.25sample. We see this in the inset to Figure 4.2(b) which shows the same data from the main panel with the x = 0.25 data superimposed as solid circles, with 0.25Å^{-2} added to make them line up with the other points in the polaronic region. The dashed line drawn through the x = 0.25 points shows power-law behavior suggesting a secondorder transition added to the transition from the Debye curve. The peak-heights from the x = 0.25 data fit this curve well over the entire range. The same function is plotted in Figure 4.2(b) as a curved dashed line and the cooling cycle points, shown as filled circles, between T_{fm} and T_{co} begin following the curve as well. The first two points below T_{fm} lie on this line, while the third point, which has just entered the charge ordered phase, is between the line and the Debye curve.

We explain the electronic behavior of the ferromagnetic phase through a coexistence of localized and delocalized charges. As we cool through T_{fm} the polaronic charges begin to delocalize and we see the local structure begin to sharpen accordingly. However, the remaining localized carriers begin ordering around 180K which stabilizes the the polaronic state. This suppresses further delocalization, and the number of delocalized carriers begins to fall until they are all back to a polaronic state. This explains why the charge ordering is originally incommensurate, since the number of carriers available for ordering is originally less than the $\frac{1}{2}$ per Mn site required to be commensurate with the lattice. However, charge ordering increases the number of localized carriers and polaron density gradually approaches 50%. Eventually, when the density of delocalized carriers becomes too small, superexchange coupling becomes favored over double exchange and ferromagnetism is lost. This point, where virtually all carriers are relocalized as polarons, as determined from the PDF coincides with the point where charge ordering becomes commensurate.

4.3 Summary

These PDF measurements allow us to understand in some detail the nature of the different phases of the $La_{1-x}Ca_xMnO_3 x = 0.5$ compound. At high temperatures the carriers are all localized but there is no charge ordering. The FM state contains a mixture of polarons and delocalized charges. It attempts to behave as the lower-

doped compounds do in this phase, by delocalizing more and more carriers as the temperature falls until it reaches a ground state where there are no polarons and the structure is undistorted. But long before it can reach this point the appearance of charge ordering stops further delocalization by creating a lower energy state for localized carriers. When all the charges relocalize the charge ordering can be fully commensurate and we arrive in the insulating ground state. The behavior of the FM state at x = 0.5 agrees with our view of the CMR region. In both cases charges delocalize in the FM phase but not instantaneously. Not until we are deep in this region do all traces of polarons disappear, but the x = 0.5 compound simply never gets that far. The low-temperature, x-dependent measurements shown in Figure 3.7 support the picture that much of the FM phase close to the MI transition boundary actually contains a large fraction of residual polarons.

Chapter 5

Discussion and Conclusions

5.1 Summary

We set out to understand the phase diagram of $La_{1-x}Ca_xMnO_3$ using local structure as our guide. In particular, we wanted to understand the mechanism behind the interesting CMR behavior these materials display. The motivation for our approach was the suggestion [23, 24] that electron-lattice effects played an important part in the properties of this class of compounds through the Jahn-Teller effect which leads to polarons in some regions of the phase diagram. Since a local structural probe is capable of detecting the distortions caused by polarons we attempted to test this idea using the atomic pair distribution function method.

5.1.1 Results

Our findings confirm that polaronic effects are important in this CMR material. In Chapter Three we showed that large changes in PDF peak heights are closely correlated with crossing the T_c / T_{mi} boundary. These changes indicate a large increase in disorder of the Mn-O₆ octahedra as the PI phase is approached and then entered. This is just the sort of distortion which would be caused by small polarons. In addition, there are large qualitative changes in the PDF upon crossing the MI transition line as a function of temperature or composition. Similar changes in T and x which do not cause a phase change create a much smaller change in the PDF. Clearly there is a connection between the structure and the electronic state, which we explain with the appearance of polarons.

At low temperatures, the FM state contains carriers which have essentially all delocalized. The structure contains no disorder and no Jahn-Teller effect is present. Models based on the average structure, containing no JT distortions, fit data in the FM state at low temperature very well but performed much worse in other parts of the phase diagram. This agreement between local and average structure means there is very little disorder in this region, hence few if any polarons. Also, at low tempearatures the peak heights in Figure 3.3 reached a saturation point. After they had risen steeply around T_c they displayed canonical behavior according to the Debye curve. This indicates that the delocalization process has stopped, presumably because there are no more carriers left as polarons. At intermediate temperatures the FM state is microscopically inhomogeneous or phase-separated. It consists of both localized and delocalized carriers. This is seen through the drop in peak height which begins much below T_c , and also through the growth of the secondary peak near 2.3Å before T_c has been achieved.

The transition from metal to insulator as a function of composition is qualitatively different from the temperature-dependent transition. We see the smooth evolution of peak heights through x_{MI} in Figure 3.7 in contrast to the dramatic effects around T_c . This suggests that x_{MI} is defined by the appearance of a percolative path of undistorted Mn ions which would allow metallic transport. Unfortunately, the poor quality of the samples involved in this experiment makes this a somewhat more tentative result at the moment. However, increase in peak height which continues until x = 0.25 does support the earlier result that much of the FM phase contains polarons as well as delocalized carriers.

We can now understand the strange phenomenology of the x = 0.5 sample. The FM transition is identical to those with x < 0.5: charges begin to delocalize but are still significantly polaronic. At T_{CO} the remaining polarons order, which lowers the energy of the localized phase. This causes the delocalized fraction to progressively reenter the polaron state until they are used up. This is the point when superexchange becomes preferred over DE and we enter the AFI state. This result supports our previous conclusions because without the ability of both types of carriers to coexist there is no way to explain ferromagnetism in the x = 0.5 compound without the carriers changing from completely localized to completely delocalized.

5.2 Future work

One of the main questions which we were unable to resolve is the exact shape of the Jahn-Teller distortion. A primary difficulty had to do with the scattering lengths of our constituent atoms. While oxygen is a fairly strong neutron scatterer which made oxygen correlations show up well, manganese has a negative neutron scattering length. Because of this, all Mn-to-other correlations have a negative sign and there is considerable cancellation of signal in the final PDF. This was one reason why we considered turning to x-rays. Obviously, a problem would then be that oxygen correlations would be overwhelmed by those of the larger atoms. However, a combination of both techniques could be succesful in solving many of these difficulties.

Figure 5.1 shows PDFs measured on $La_{0.75}Ca_{0.25}MnO_3$ using neutrons and xrays. Some of the most prominent features in each PDF are barely present in their counterpart. This is not an experimental artifact but the result of very different scattering properties when x-rays are substituted for neutrons. Since Lanthanum



Figure 5.1: PDFs of $La_{0.75}Ca_{0.25}MnO_3$ measured at room temperature using x-rays and neutrons.

correlations dominate the x-ray PDF, these data could be used to pin down the structure of the La/Ca sublattice. Once these positions are known, they could be used when modeling a neutron PDF. This should produce a better model and reduce the number of variables to be refined. We then would stand a better chance at being able to fit the shape of the Jahn-Teller distortion.

Another experiment that should be performed is to re-measure PDFs at base temperature for compounds with x-values closely spaced from 0 to 0.33. While difficulties persist in obtaining homogeneous samples in sufficent quantities for neutron diffraction, this remains an important piece of work. If we can confirm our results from our first attempt it would not only support the percolative model of conduction, but boost all of our previous results. If the peak heights show a large response at x_{MI} , this would force us to reexamine many of our ideas.

APPENDIX

Publications:

S. J. L. Billinge, R. G. DiFrancesco, M. F. Hundley, J. D. Thompson, and G. H. Kwei, Competition between charge localization and delocalization in $La_{0.50}Ca_{0.50}MnO_3$, *Phys. Rev. Lett.*, submitted to Phys. Rev. Lett. (2000)

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