Relationship between macroscopic physical properties and local distortions of low doping La$_{1-x}$Ca$_x$MnO$_3$: an EXAFS study

Y. Jiang,$^1$ F. Bridges,$^1$ L. Downward,$^1$ and J. J. Neumeier$^2$

$^1$Physics Department, University of California, Santa Cruz, California 95064, USA
$^2$Department of Physics, Montana State University, Bozeman, Montana 59717, USA

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Abstract

A temperature-dependent EXAFS investigation of La\(_{1-x}\)Ca\(_x\)MnO\(_3\) is presented for the concentration range that spans the ferromagnetic-insulator (FMI) to ferromagnetic-metal (FMM) transition region, \(x = 0.16, 0.18, 0.20,\) and \(0.22;\) the titrated hole concentrations are slightly higher \(y = 0.2, 0.22, 0.24,\) and \(0.25\) respectively. For this range of Ca concentrations the samples are insulating for \(x = 0.16-0.2\) and show a metal/insulator transition for \(x = 0.22.\) All samples are ferromagnetic although the saturation magnetization for the 16% Ca sample is only \(\sim 70\%\) of the expected value at 0.4T. This raises a question as to the nature of the ferromagnetic (FM) coupling mechanism in such insulating samples. We find that the FMI samples have similar correlations between changes in the local Mn-O distortions and the magnetization as observed previously for the colossal magnetoresistance (CMR) samples \((0.2 \leq x \leq 0.5)\) - except that the FMI samples never become fully magnetized. The data show that there are at least two distinct types of distortions. The initial distortions removed as the insulating sample becomes magnetized are small and provides direct evidence that roughly 50\% of the Mn sites (associated with the hole charge carriers) have a small distortion/site and are magnetized first. The large Mn-O distortions that remain at low T are attributed to a small fraction \(< 30\%)\) of fully Jahn-Teller-distorted Mn sites that are either unmagnetized or antiferromagnetically ordered. Thus the insulating samples are very similar to the behavior of the CMR samples up to the point at which the M/I transition occurs for the CMR materials. The lack of metallic conductivity for \(x \leq 0.2,\) when 50\% or more of the sample is magnetic, implies that there must be preferred magnetized Mn sites (that involve holes) and that such sites do not percolate at these concentrations.

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I. INTRODUCTION

LaMnO$_3$ is an antiferromagnetic insulator and has a large Jahn-Teller (J-T) distortion of the MnO$_6$ octahedron. When it’s doped with Ca on the La sites (i.e. La$_{1-x}$Ca$_x$MnO$_3$ (LCMO)), holes are introduced into the Mn $e_g$ band and this leads to novel transport and magnetic properties including colossal magnetoresistance (CMR) and ferromagnetism for samples with Ca concentrations, $x$, roughly in the range 20-50%.$^{1,2,3}$ In this concentration range, these pseudo-cubic manganites are paramagnetic insulators (semiconductors) at high T, with a significant distortion of the Mn-O octahedron (for some sites) that is associated with Jahn-Teller distortions and polarons. Upon lowering the temperature below the ferromagnetic transition temperature $T_c$, the Mn spins begin to align and thus the holes (electrons) can hop more rapidly between Mn atoms without a spin flip via the intervening O atom; this enhances the ferromagnetic (FM) coupling between Mn spins and is referred to as the double exchange (DE) interaction.$^{4,5,6}$ To explain the large magnetoresistance a polaron-like lattice distortion must also be present.$^{7,8,9,10,11}$ A consequence of very fast hopping of holes between neighboring Mn sites is that the broadening, $\sigma$, of the Mn-O pair distribution function (PDF) is greatly reduced when the sample becomes magnetic, thus $\sigma^2(T)$ decreases rapidly below the ferromagnetic transition temperature $T_c$. Finally, at low T, LCMO in the CMR regime is a ferromagnetic metal with very little static distortion of the Mn-O bonds.$^{12,13,14}$

For LCMO in this concentration range ($x \sim 0.2 - 0.5$), Downward et al.$^{14}$ have shown that there is a strong correlation between the local Mn-O distortions removed, $D = \Delta(\sigma^2)$, and the magnetization, as $T$ is lowered through and below $T_c$. By plotting $D$ (for the Mn-O PDF) versus the sample magnetization, Downward et al.$^{14}$ found that $D$ increases slowly with $M$ until $M/M_0 \sim 2x$ ($M_0$ is the saturation magnetization at low T); for larger $M$, $D$ increases more rapidly. The low initial slope in such a plot is direct experimental evidence of sites with a low distortion/site, while the large slope ($\sim 4$ times larger) at high $M$ indicates that the remaining small fraction of Mn sites have a large distortion/site. Thus there are at least two different types of distortion present, which have only been distinguished (so far) by correlating with magnetization. An important question is - can one of the regimes be made more dominant by appropriate doping, so that this effect is more directly observable? We will address that issue in this paper.
Because the fraction of low distortion sites is roughly 2x, Downward et al.\textsuperscript{14} proposed a two-site polaron model (called a dimeron) in which a hole is partially delocalized over two Mn sites [initially one Mn site would correspond to an $e_g$ electron site (Mn$^{+3}$) while the other would correspond to a hole site (Mn$^{+4}$)]. The magnetization, M, first develops via the aggregation of these low-distortion dimeron sites (or multiples of such pairs). The argument for a lower distortion of the dimeron is that when the hole (or electron) is partially delocalized – a dynamic effect, the average charge per site is reduced to 3.5 (from 4 electrons on an isolated Mn$^{+3}$ site) and J-T energies are reduced.

In this model for $M/M_0 > 2x$, further increases in $M$ (induced by either lowering T or increasing B) force the remaining J-T-distorted Mn sites, each containing one $e_g$ electron, to become magnetized. If the hole quasiparticles now spend time on such sites, a large J-T distortion per Mn site is removed as observed for CMR samples\textsuperscript{14}. In fact, most of the distortion removed in the FM state for CMR samples occurs after the sample is more than 50% magnetized. Consequently, if the sample never became fully magnetized, e.g. for the lower Ca concentrations considered here, the remaining net Mn-O distortion at low T should be much larger than has been observed for the CMR regime. Note that in the partially magnetized state at low M there will be three types of Mn sites - i) undistorted sites in the developing magnetic regions, ii) low distortion sites corresponding to the remaining dimerons (polarons) that are not yet part of a magnetic cluster, and iii) highly distorted Mn$^{+3}$ sites.

In considering how double exchange leads to both ferromagnetism and a disappearance of local Mn-O distortions, an important question to ask is how many Mn sites can one hole keep undistorted by hopping rapidly between them in the ferromagnetic metallic phase? The answer appears to be about four. For the 25% Ca samples, there are four sites/hole, (for higher Ca concentrations fewer sites/hole). The material is ferromagnetic and there is little excess distortion at low T for $x$ between 25 and 40\%\textsuperscript{13,14} - the Mn-O distortion at low T approaches the zero-point-motion value comparable to that observed in CaMnO$_3$. For lower Ca concentrations, there is an increasing amount of distortion at low T and at $x = 0.21$ the sample does not become fully magnetic even at moderate fields (0.4T)\textsuperscript{14}. Thus in this case the holes do not get to every site often enough to maintain all the sites at a low distortion.

A related point is that dynamics plays an important role; if the holes hop fairly rapidly
above $T_c$ - at least among a few sites - then there will be no Mn$^{+4}$ sites in the sample over the time scale of most experiments. Thus characteristics of a particular site becomes a time average of a hole site and an electron site as holes hop on and off that particular site. This will depend on the time scale of the measurements and the hole hopping rate; the latter exceeds optical phonon frequencies in the FMM regime. When the hole is present the site becomes less distorted, whereas when an $e_g$ electron is present it will become more distorted; consequently, rapid hopping at the local level will produce a lower net distortion per site, at least for some sites.

At lower Ca concentrations it is well known that the material becomes a ferromagnetic insulator (semiconductor) at low $T$. An important detail is that these samples are never fully magnetized in moderate fields at low $T$, and the unmagnetized fraction increases slowly as the Ca concentration decreases below $\sim 20\%$ Ca. Since LCMO is a soft ferromagnet for higher Ca concentrations it is fully magnetized at low $T$ for moderate fields (0.4T)$^{14,15}$ and as we will show, for all the samples that have a M/I transition. At lower Ca concentrations ($x \sim 0.1$) a canted AFM state exists$^{16,17}$ but disappears near $x = 0.125$. However that does not preclude tiny AFM coupled clusters a few nm in size whose size diminishes as $x$ approaches 0.22. Thus the nature of the magnetic structure is not well understood in this concentration range.

At first ferromagnetism in an insulator appears to be in contradiction to a DE model$^{18,19,20}$ because for double exchange, the Mn spins are ferromagnetically coupled via fast hopping of the holes (or $e_g$ electrons) between Mn sites in the metallic regime. Some have suggested a mixture of (DE) ferromagnetic metallic, and ferromagnetic insulating (distorted and non-conducting) phases$^{19,21,22}$ but that requires invoking a new FM coupling mechanism (FM superexchange) for the FMI phase (for only a tiny change in Ca concentration), although the superexchange mechanism is normally AFM in LaMnO$_3$. That may well be necessary at low concentrations ($x = 0.1$) where there are not enough holes to couple all the Mn sites via DE (the ratio is now 10 Mn sites/hole). Interestingly, the $x = 0.1$ sample can be made completely ferromagnetic but non-conducting in a 12T field$^{22}$ however in that case there should be a significant fraction of the sample that is magnetized and yet retains a large J-T distortion since the latter is only removed if the hole quasiparticles are hopping rapidly over all the sites. One alternative explanation for a low magnetization at moderate fields for concentrations near 16-20% is that FM (conducting) domains do form but are sep-
arated by insulating, non-ferromagnetic regions (possibly tiny antiferromagnetically coupled clusters or a frustrated spin-glass-like configuration as a result of competing FM and AFM magnetic interactions for some sites). In either case, for x near 20% a small fraction of the sample appears to block the metallic conductivity and appears to be due to the intrinsic inhomogeneity of the sample at the unit cell level.

Several other papers also speak to this inhomogeneity. Electron magnetic resonance (EMR) studies\textsuperscript{23,24} indicate multiple phases in a sample close to the concentration-driven MI transition. For x = 0.18 and 0.2 they observe at least three resonance lines\textsuperscript{24} which they attribute to different phases just below T\textsubscript{c} - a ferromagnetic metallic phase and two distinct ferromagnetic insulating phases. Other investigations at low Ca concentrations suggest that Mn\textsuperscript{+4} hole sites may be localized. Alonso \textit{et al.}\textsuperscript{15} argue that in such samples the conductive properties depend on the origin of the holes - from metal atom vacancies or from Ca dopants; the samples need Ca dopants to be conducting at higher concentrations. They propose that localized Mn\textsuperscript{+4} hole sites form close to the Ca dopants which leads to unconnected magnetic/metallic clusters at low Ca concentrations; they also suggest that perhaps the J-T distortions of Mn\textsuperscript{+3} sites near the Ca\textsuperscript{+2} dopants are smaller than near La\textsuperscript{+3}, but they do not provide a well defined model. Algarabel \textit{et al.}\textsuperscript{22} also suggest that holes are likely found close to the Ca sites in low concentration samples. Finally, in zero-field NMR experiments using low Ca concentration samples, at least 3 distinct regions with different hyperfine fields at the Mn nuclei have been observed, but only at very low T when the magnetization has reached it’s maximum value\textsuperscript{21}; they do not report results in the temperature regime (100-200K) over which most of the magnetization develops. They argue that a significant fraction of (localized) Mn\textsuperscript{+4} are FM coupled. This requires a different FM coupling mechanism to produce insulating FM Mn\textsuperscript{+4} sites and essentially no hopping of such holes.

Finally it should be noted that diffraction studies\textsuperscript{16,17} suggest a transition for low Ca concentrations from a high temperature pseudo-cubic to a low temperature, lower symmetry phase, with the transition between 200-400K. Biotteau \textit{et al.}\textsuperscript{16} interpreted this transition as an evolution from a dynamic Jahn-Teller effect (high T) to a cooperative static J-T distortion (Space group \textit{Pbnm}) at lower T. A more recent paper\textsuperscript{17} describes this transition as a symmetry change at T\textsubscript{J-T} from \textit{P21/c} at low T to orthorhombic (\textit{Pnma}) at high T. For example, for the x = 0.175 sample, Pissas \textit{et al.}\textsuperscript{17} show that the separation of the Mn2-O bond lengths is a maximum near 200K for \textit{P21/c}; the distribution of bond lengths narrows
slightly at low T but collapses to essentially one bond length at 300K. This is in contrast to the EXAFS results we present here. EXAFS is a very fast probe (10^{-15} \text{ sec}) and can see similar J-T distortions in either the dynamic or static regime. We discuss these and other results mentioned above, in the discussion section.

So far, there have been few local structure studies done for lower Ca concentration samples, though we have previously shown\textsuperscript{13} that the distortion removed as the sample becomes magnetized, is small for a low concentration, x \sim 0.12. However, for samples at the boundary between the ferromagnetic insulator region (Ca concentration below 20\%) and the CMR region (Ca concentration \sim 20-50\%), no local structure experiments have been done to explore the relationship between distortions removed and the sample magnetization. Here, we present a detailed EXAFS study through the concentration driven metal/insulator transition. We find similar behavior as for LCMO with higher Ca concentrations, but the total distortion removed in the FM insulating state at low T is greatly reduced. Specifically, in a comparison of 4 different samples [Ca concentrations 0.16 - 0.22; effective hole concentrations y = 0.2 - 0.25] we find that the total magnitude of the local Mn-O distortions removed in the FM state, decreases rapidly (by more than a factor of 2) when the metal/insulator transition disappears in the resistivity data. For the insulating samples, the small overall change in \sigma^2(T) as the sample becomes magnetized is direct evidence that a large number of Mn sites (at least 50\%) have a low distortion per site at T\_c.

This paper is organized as follows: a brief description of the sample preparation and the EXAFS techniques are presented in Sec. II, the magnetization and resistivity data are presented in Sec. III, and then the EXAFS data and analysis are discussed in Sec. IV. A comparison with the model of Downward \textit{et al.}\textsuperscript{14} and with other results is provided in Sec. V.

II. EXPERIMENTAL DETAILS AND THE EXAFS TECHNIQUE

Transmission EXAFS Mn K-edge data were collected over a wide temperature range (3-550K) on powdered samples at the Stanford Synchrotron Radiation Laboratory (SSRL). A cryostat was used to collect the low temperature (3-300K) data at beamlines 10-2 and 2-3 using both Si(111) and Si(220) monochromators, and an oven was used for the high temperature (300-550K) data at beamline 2-3 using a Si(111) monochromator. To reduce
the harmonic content in the X-ray beam, we detuned the monochromator crystals 50%, and also used a harmonic rejection mirror for the Si(220) monochromator on 10-2. The samples are oriented 90 degree to the x-ray beams. The energy resolution (δE) is 1.0 eV for the Si(111) monochromator and 0.44 eV for the Si(220) monochromator.

Samples of La$_{1-x}$Ca$_x$MnO$_3$ with $x = 0.16$, 0.18, 0.20, and 0.22 were made by weight appropriate amounts of 99.99% purity or better La$_2$O$_3$, CaCO$_3$, and MnO$_2$, mixing with a mortar and pestle for 10 min, and reacting for 3 h at 1150°C in air in an alumina crucible. The samples were removed from the furnace, reground for 10 min, and reacted for 16 h at 1250°C. This last step was repeated 5 times with reaction temperatures of 1300°C, 1350°C, 1375°C (twice) and 1400°C in air. The samples were then reground for 10 min, pressed into pellets, and reacted for 16 h at 1400°C. The as-made samples, $x = 0.18$-0.22, showed a metal/insulator transition and had excess oxygen (i.e. a few metal atom vacancies). To lower the O concentration, pressed pellets of the samples were placed in a flow of Ar gas for 12 h at 1250°C. Iodometric titration was used to determine the final average Mn valence which was found to be 3.20(1), 3.22(1), 3.23(1) and 3.25(1) for $x = 0.16$, 0.18, 0.20, and 0.22, respectively. The excess O is about 0.015 (i.e. O$_{0.015}$), or in terms of metal site vacancies, the composition would be approximately (La$_{1-x}$Ca$_x$)$_{0.994}$Mn$_{0.994}$O$_3$. Thus the non-stoichiometry is very small. Powder x-ray diffraction revealed the single phase nature of the samples.

Magnetization versus T was measured in a magnetic field of 0.4T for most samples (0.2T for the as made 0.16 and 0.18 samples); M vs B data were also collected at low T. The electrical resistivity was measured on small bars cut from the pressed pellet (1mm X 1mm X 6mm) using a four-probe dc technique.

To prepare EXAFS samples, the pressed pellets were ground in a mortar and pestle, passed through a 400-mesh sieve, and then brushed onto scotch tape for the cryostat measurement, or onto kapton tape for the oven measurement. The tape preferentially holds the smaller grains ($\leq 5\mu m$) in a thin layer; two double layers of tape were used for these EXAFS measurement.

Fits of the EXAFS data were carried out to the real and imaginary functions in r-space (the Fourier Transform of $k\chi(k)$), using the EXAFS equation for $k\chi(k)$ which is given by:
\[ k \chi (k) = \sum_i k \chi_i (k) \]

\[ = Im \sum_i A_i \int_0^\infty F_i(k,r) \frac{g_i(r_{0i},r)e^{i(2kr+2\delta_c(k)+\delta_i(k))}}{r^2} dr \]

(1)

\[ A_i = N_i S_0^2, \]

(2)

where \( g_i(r_{0i},r) \) is the \( i^{th} \) shell pair distribution function (PDF) for atoms at a distance \( r_{0i} \) from the center atom, (here Mn), \( F_i(k,r) \) is the backscattering amplitude, and \( \delta_c(k) \) and \( \delta_i(k) \) are the phase shifts from the central and backscattering atom potentials respectively. The amplitude, \( A_i \) (Equ. 2), is the product of the coordination number, \( N_i \), from diffraction and \( S_0^2 \), the amplitude reduction factor, which is included to correct for multi-electron effects since multi-electron processes contribute to the edge step-height but not to the EXAFS amplitude. Experimentally, \( S_0^2 \) also corrects for several other small effects such as small errors in the estimation of the mean free path in the theoretical calculations, a small amplitude reduction in the data because of the X-ray energy resolution, some harmonic content in the synchrotron beam, non-uniformity/pinholes in powder samples, etc. Finally an additional parameter, \( \Delta E_0 \), describes the difference in edge energy between the value defined for the data (half height) and the theoretical functions (for which \( k = 0 \) at \( E_0 \)).

Since the EXAFS measurements were collected on two different beamlines with different energy resolutions and with two different set-ups for the low and high-T ranges, there will be slight variations in the amplitude reduction factor (and we have to choose two slightly different \( S_0^2 \) for each set of data). Further discussion about setting \( S_0^2 \) will be given later.

In fitting the EXAFS data, we assume a Gaussian PDF with a width \( \sigma \) for the first shell Mn-O peak. Also note that different contributions to \( \sigma^2 \) add up in quadrature if the different distortion mechanisms are uncorrelated; i.e. \( \sigma_{total}^2 = \sigma_{phonons}^2 + \sigma_{static}^2 + \sigma_{polarons}^2 + \sigma_{J-T}^2 \). According to the model proposed by Downward et al., near \( T_c \) a fraction 2\( y \) of the sites are covered by two-site polarons (dimerons) \( (\sigma_{polarons}^2) \) and the remaining \( (1-2y) \) are J-T distorted electron sites \( (\sigma_{J-T}^2) \). These two contributions are summed to give \( \sigma_{J-T/polarons}^2 \); this quantity will vary with magnetization (and temperature) as first the dimerons, and at lower \( T \), the more distorted J-T sites, become magnetized.
FIG. 1: Magnetization as a function of B-field and temperature: a) M vs B for the as made samples (5K), b) M vs B for the annealed samples (5K), c) M vs T for the as-made samples (0.4T for x = 0.2, 0.22; 0.2T for x = 0.16, 0.18) and d) M vs T after annealing in Ar (0.4T). These figures show that the magnetization is highest at low T and is fairly close to the theoretically expected value for the as-made samples. For the annealed samples the saturation magnetization is smaller, and significantly reduced for the 16% Ca sample at 0.4T. Only at high B-fields does M approach the saturated value. The number of data points plotted is reduced to 200 for each curve for clarity.

III. MAGNETIZATION AND RESISTIVITY DATA

The magnetization, M, is plotted as a function of B in Fig. 1a,b for the as made and Ar annealed samples respectively. These plots show the evolution of the magnetization process as the hole concentration is lowered. The as made samples have reached saturation at or below 0.4T as observed previously for CMR samples. However for the Ar annealed
samples the curves are spread out over a range of B-fields. Although the x = 0.22 sample also saturates below 0.4T, the other samples significantly larger magnetic fields to reach saturation, and M is still increasing at 1T for the x = 0.16 and 0.18 samples. An important question here is whether the lower magnetization at 0.4T means that some sites are not yet magnetized or that all the Mn spins are magnetized but some sites are in non-aligned clusters. We argue that it is likely the former. First for all CMR samples the DE coupled FM sites are easily aligned at 0.4T and the same should apply for the main FM domains for slightly lower Ca concentrations. However as the Ca concentration decreases there will be an increasing number of tiny regions with no Ca, and hence no local holes. These nanoscale regions, of order a few unit cells, will possess mostly AFM coupling between a few Mn sites (but no long range AFM order) since that is the dominant magnetic coupling when no holes are present. In addition there will be Mn spins on the boundary between these AFM-coupled nanoclusters and the large FM clusters. Such spins may be frustrated - having AFM coupling to the nano AFM cluster but FM coupling to the FM clusters as a result of occasional hole hopping onto these sites. Consequently the boundary Mn sites and the AFM coupled nano-clusters may not be aligned at low B fields, but can be forced to align at high B-fields. The structural results obtained from the EXAFS results below supports this scenario and will be discussed in more detail later.

Fig. 1c,d shows the magnetization, M, as a function of T before (Fig. 1c) and after (Fig. 1d) the anneal in Ar to reduce the O content - the Ca and final hole concentrations are x = 0.16, 0.18, 0.2, and 0.22, and y = 0.2, 0.22, 0.23, and 0.25 respectively. Note that the values of $T_c$ are reduced by 15-20K after the anneal for each concentration. For each plot the saturation magnetization decreases as the Ca concentration decreases whereas a very slight increase is expected ($M_{sat} = (4-x)\mu_B$); more importantly, the saturation magnetization in the annealed samples is significantly reduced at 0.4T as discussed above. For the as-made samples the saturation magnetization at low T in these plots is low for the x = 0.16 and 0.18 samples because these data were collected at 0.2T instead of 0.4T prior to annealing. For the Ar annealed samples, the saturation magnetization for the 16% Ca sample drops by $\sim$30% at 4K (B = 0.4T) compared to the 22% sample (Fig. 1d).

In Fig. 2, the resistivity is plotted for the as-made (Fig. 2a) and annealed (Fig. 2b) samples. For the as-made samples, the M/I transition occurs between 0.16 and 0.18 Ca concentration, and $\rho(T)$ varies significantly near $T_c$. After the reduction of oxygen via the
Ar anneal, the resistivity increases considerably and only the 22% Ca sample shows a M/I transition. From the above data, the annealed samples are mostly in the FM insulator regime and thus are the more important samples for this study. Note that the small reduction in O content has a significant change in the bulk magnetization for the x = 0.16 sample.

IV. EXAFS DATA AND ANALYSIS

The EXAFS data were reduced using the RSXAP package which implements standard data reduction techniques. A pre-edge background was removed from the data (the Victoreen formula was used to adjust the slope above the edge after the pre-edge subtraction) and an experimental $E_0$ was defined as the energy of the half-height point on the Mn K-edge. The
post-edge background was removed using a spline with five knots to approximate $\mu_0$ in
$\mu(E) = \mu_0(1 + \chi(E))$. The background-subtracted data $\chi(E)$ were then transformed to
k-space using the relation $k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$.

Next the k-space data $k\chi(k)$ were Fast Fourier Transformed (FFT) to r-space with a
k-space window of 3.3-12.0 $\text{Å}^{-1}$ with a Gaussian broadening of width 0.2 $\text{Å}^{-1}$. Examples of
the data are shown in Fig. 3 for two annealed samples ($x = 0.16$ and 0.22).

The data were then fit to theoretical EXAFS functions generated by FEFF 8.20 (developed by Rehr and co-workers$^{26}$), using the program rsfit (RSXAP package). Our primary
interest here is the width of the Mn-O PDF which parametrizes the amount of distortion
present. We used only one value of $\sigma$ for the Mn-O shell as in previous work$^{14}$ and fixed
the number of oxygen neighbors to the lattice structure ($N_1 = 6$ neighbors) for each sample.

To get a reasonable fit, a number of other constraints on the parameters are also required.
First, for data collected on the same sample and on the same beamline, $\Delta E_0$ was obtained
by allowing $\sigma$ and $\Delta E_0$ to vary on the lowest temperature data; the average value obtained
from those fits was used to constrain $\Delta E_0$ for the rest of the data in the same set. For the
parameter $S_0^2$, a number of fits were carried out. In the first set of fits, we let the amplitude
$A_1$ ($A_1 = N_1 S_0^2$) vary for the low temperature data and determined $S_0^2$ from those fits.
Then $A_1$ was kept constant for fits as a function of T. The main effect of small changes in
this parameter is a vertical shift of plots of $\sigma^2$ versus T. Once $S_0^2$ for the low temperature
data (3-300 K) was determined, we slightly adjusted $S_0^2$ for the high temperature data set
(300-550K) to make the values of $\sigma^2$ align with the low T data at 300K. For all the data
below 330K, $S_0^2 \approx 0.75$; the variation to join high T and low T data is $\approx 0.01$.

Most of the data were collected on the Ar annealed samples but a few points were collected
on two of the as-made samples. In Fig. $\Box$ $\sigma^2$ is plotted (on different expanded scales) as a
function of T before and after the anneal for $x = 0.16$ and 0.22. Although the data for the
as-made samples are sparse (solid points), it is clear that after annealing there is a shift of
$T_c$ to lower T for both samples (See also Figs. $\Box$ and $\Box$) and that the step-height decreases,
particularly for the $x = 0.22$ sample.

Fig. $\Box$ shows $\sigma^2(T)$ for all the annealed samples on the same scale. The step increase in $\sigma^2$
is sharp near $T_c$ for the $x = 0.22$ ($y = 0.25$) sample and has a comparable (slightly smaller)
step height to that observed in other CMR samples$^{14}$ As before, we attribute this step to
a large increase in the distortions of the Mn-O bonds, associated with dimerons (extended
FIG. 3: (Color online) A comparison of EXAFS data for the $x = 0.16$ and 0.22 samples after annealing (hole concentrations are $y = 0.20$ and 0.25 respectively). Top: k-space data for $x = 0.22$, Middle: r-space data for $x = 0.22$; Bottom: r-space data for $x = 0.16$. In each case, the amplitude is highest at low temperature and decreases monotonically with increasing temperature. Note that the amplitude for the $x = 0.16$ sample (Bottom) is smaller overall (more disorder) and has a weaker $T$ dependence compared to the $x = 0.22$ sample (Middle).
FIG. 4: \( \sigma^2 \) as a function of T for: (a) \( x = 0.16 \); and (b) \( x = 0.22 \) samples, before and after the Ar anneal. The anneal shifts the step in \( \sigma^2 \) (near \( T_c \)) to lower temperatures and the height of the step is reduced. Note the different vertical scales used for (a) and (b).

polarons with low distortions) and some more isolated, highly J-T distorted electron sites, as the temperature is increased through \( T_c \). However, the other three samples (\( x = 0.16-0.20 \)) have a much smaller step near \( T_c \), which decrease slightly with smaller \( x \), and a much larger value of \( \sigma^2 \) remains at low T. Thus even though a large fraction of the sample is magnetized (70% or more), only a small distortion is removed in the FM phase for these samples. A significant fraction of the sample (up to \( \sim 30\% \) for \( x = 0.16 \)) remains distorted at the lowest temperatures (Note: \( \sigma^2(4K) \) is well above the value for zero-point motion). There is also an increased static distortion above \( T_c \) for the insulating samples.

In addition, the temperature dependence of \( \sigma^2(T) \) above \( T_c \) is comparable for all samples. The thermal phonon contributions were determined from a fit of \( \sigma^2(T) \) above \( T_c \) (205-550K) to the correlated Debye model (Equ. 3) plus a static off-set. This model is usually a good approximation for all phonon modes\(^{27}\) including acoustic and optical phonons and is given by:\(^{28,29,30}\)

\[
\sigma^2_{\text{Debye}} = \frac{3\hbar}{2MR} \int_0^{\omega_D} \frac{\omega}{\omega^3_D} C_{ij} \coth\left(\frac{\hbar \omega}{2k_B T}\right) d\omega; \tag{3}
\]

where \( \omega_D \) is the Debye frequency, \( C_{ij} \) is a correlation function given by \( 1-\sin(\omega r_{ij}/c)/(\omega r_{ij}/c) \), 

\[
c = \frac{\omega_D}{k_D}
\]

where \( k_D \) is the Debye wavelength, and \( \sigma^2_{\text{Debye}}(T \sim 0) \) with zero static offset gives the zero-point motion value of \( \sigma^2 \). The slope of \( \sigma^2_{\text{Debye}}(T) \) vs T is very low at low T and
FIG. 5: $\sigma^2$ as a function of T for the four annealed samples (x = 0.16 - 0.22) on the same vertical scale. The plot of the x = 0.22 sample is similar to previous samples which show a M/I transition, however, the other three samples, which all show insulating behavior and a reduced saturation magnetization at low T, have a significantly smaller step in $\sigma^2$ and a slightly increased distortion above $T_c$ (higher $\sigma^2$) than other CMR samples.

increases to a constant value (determined by the spring constant, reduced mass, and $C_{ij}$) for $T > \Theta_D$. See Ref. 29 for details.

We obtained values of $\Theta_D \sim 812-860$K ± 30K for the four samples with an average of about 830K. This agrees well with the value $\Theta_D = 860$ K for the Mn-O bond in Ca-substituted LaMnO$_3$ materials as obtained previously. This fit passes through the points above $T_c$ (T > 200K) very well. In Fig. 6, we plot the results for x = 0.22 and the Debye curve ($\Theta_D = 830$K) with the static contribution removed. This represents the thermal contribution to $\sigma^2$ (including zero-point-motion); notice that this curve is parallel to the data above $T_c$.

The non-thermal-phonon contribution to $\sigma^2$ that is removed as the sample is cooled below $T_c$, $\sigma_{J-T/polaron}^2(T)$, can be obtained by subtracting the Debye curve (solid line in Fig. 6) from the $\sigma^2(T)$ data for each sample. The results are shown in Fig. 7. This plot illustrates several important aspects of $\sigma_{J-T/polaron}^2(T)$. First, above $T_c$ it is independent of T - the polaron and J-T distortions are fully formed and do not change significantly with T. Second, the step decrease as T goes to zero is greatly diminished for the insulating samples, although the samples are still highly magnetic (see Fig. 1). Third (and related to the second
FIG. 6: $\sigma^2$ vs T for LCMO, x = 0.22. The solid line is the phonon contribution calculated using the correlated Debye model with zero static distortion and $\theta_D = 830$ K ($\theta_D$ for all the samples above $T_c$ varies from 812 K to 860 K with an average of about 830 K). $\sigma^2_{J-T/polaron}(T)$ - the J-T/polaron contribution - is defined as the difference between the experimental data and the phonon contribution at each temperature point.

The remaining static distortion increases as the Ca concentration is lowered, and as the fraction of sample that remains unmagnetized at 0.4T, increases.

To investigate the correlations between local structure and magnetization, we plot the data in a new way which simplifies the discussion. By combining $\sigma^2_{J-T/polaron}(T)$ (Fig. 7) with the M(T) data (Fig. 11) we plot $\sigma^2_{J-T/polaron}(T)$ vs $M/M_0$ for the four samples in Fig. 8. Here we use the fraction $M/M_0$ ($M_0$ is the theoretical saturation magnetization) as an approximate measure of the fraction of magnetized states. At low M, $\sigma^2_{J-T/polaron}$ decreases slowly with M, i.e. the distortion removed per Mn site is very small until the sample is at least 50% magnetized. At higher magnetization, $\sigma^2_{J-T/polaron}$ drops much more rapidly with M and approaches zero for the 22% sample. However for the insulating samples, relatively little distortion is removed overall. Note that the slope at low M is similar for all samples, but the 20% and 22% samples have a continuous change in slope. Here we need to point out one caveat - the EXAFS data were collected at B = 0T, while the magnetization data were collected at B = 0.4T. However, we note that while this field is large enough to be reflective of the bulk, zero-field, magnetization, it is small enough to have a minimal effect on the magnetoresistance.
FIG. 7: $\sigma^2_{J-T/polaron}(T)$ vs temperature for LCMO x=16-22%. The non-thermal contribution, $\sigma^2_{J-T/polaron}(T)$, is defined in Fig. 6. Note that above $T_c$ the $\sigma^2_{J-T/polaron}$ is independent of $T$, and that as the concentration decreases the remaining distortion at low $T$ increases.

Recently Downward et al.\cite{14,32} have shown using EXAFS measurements as a function of magnetic field for four samples from 21-45% Ca, that a universal relationship between the local distortions and the magnetization only exists for high applied B-fields e.g. $B > 2T$. At much lower B fields, domain effects are important and the observed bulk magnetization is lower than expected for the number of magnetized sites implied from the EXAFS data. This analysis suggest that the steeper the M(T) plot, the more curved the $\sigma^2_{J-T/polaron}(T)$ vs $\frac{M}{M_0}$ plot becomes. For the samples considered here, M(T) for the 16 and 18% samples have a slower $T$ dependence than the other samples. It is only for these samples that a clear break point near $\frac{M}{M_0} \sim 0.5-0.6$ is present in Fig. 8 as observed previously for the higher Ca concentrations.\cite{14}
Surprisingly the magnitude of the slope at low M for the 16% Ca sample (0.0014 Å²) is a factor of two lower than for the 30% Ca sample. For comparison, the latter data are replotted here, below the data for the 16% sample (Fig. 8); this indicates that the initial magnetized sites have even less distortion than for the CMR samples. Note that the high M slopes for the low Ca concentration samples (x = 0.16, 0.18) are comparable (within 25%) to that for the CMR samples. See Table I for a comparison of the high and low slopes with earlier results for CMR samples x = 0.21 and 0.3.

One possibility for the smaller low slope for the FMI samples is that the holes are confined...
to a smaller number of sites and hop rapidly between only a few Mn atoms, keeping them relatively undistorted. A major difference for this 16% Ca sample is that the magnetization only reaches $M/M_0 \sim 0.7$ at low $T$ and $B = 0.4T$. If one extrapolates the straight line through the data from $M/M_0 = 0.5$ to $M/M_0 = 1.0$, the distortion that would have been removed if every site became magnetized via DE, is nearly a factor of 2 larger (see dotted line for the 16% Ca sample in Fig. 8). The remaining J-T/polaron distortion at $M/M_0 = 1.0$, $\sigma_{J-T/polaron}^2 \sim 1.5 \times 10^{-3} \text{Å}^2$, is comparable to the excess distortion observed above $T_c$ (Fig. 5) within our uncertainties (in comparison, $\sigma_{J-T/polaron}^2 \sim 0$ for the 30% sample at $M/M_0 = 1.0$). Thus it is as if the magnetization process were truncated for the lower concentration samples before all sites became magnetized.

The small overall distortion removed in the FMI phase for $x = 0.16-0.2$, provides direct evidence that low distortion (non-magnetized) Mn sites associated with the charge carriers, exist at $T_c$ and are magnetized first. These are the dimeron quasiparticles proposed by Downward et al.\textsuperscript{14} This further supports the proposal that there are at least two types of distorted sites in this system: one associated with the delocalized hole charge carriers (dimeron or two-site polaron) and another with the remaining J-T distorted Mn sites.

V. DISCUSSION AND CONCLUSIONS

The first issue to discuss is the structure of these systems above $T_c$. Neutron diffraction studies show that between 200 and 300K the samples become pseudo-cubic and the Mn-O bond lengths are nearly equal above a temperature $T_{J-T}$, at these Ca concentrations\textsuperscript{16,17}. In contrast $\sigma_{J-T/polaron}^2$ from EXAFS shown in Fig. 7 has a large distortion of the Mn-O PDF above $T_c$, and it remains constant up to 400K. Biotteau et al.\textsuperscript{16} ascribe this transition

| Concentration | Low slope ($10^{-3}$Å$^2$) | High slope ($10^{-3}$Å$^2$) | breakpoint | chisq/ndf |
|---------------|-----------------------------|-----------------------------|------------|-----------|
| 16%           | -1.44                       | -6.84                       | 0.517      | 0.790     |
| 18%           | -1.41                       | -6.29                       | 0.621      | 1.061     |
| 21%           | -3.18                       | -6.31                       | 0.611      | 4.497     |
| 30%           | -2.95                       | -8.65                       | 0.678      | 2.123     |
to a change from a quasi-static to a dynamic J-T effect. We agree with this assignment - EXAFS is a very fast probe (∼10^{-15} s) and can follow any structural J-T distortions. The constant value of σ_{J-T/polaron}^2(T) above T_c means that the magnitude of the J-T distortion is unchanged. The collapse of the Mn-O PDF observed in neutron diffraction means that the lattice fluctuations associated with J-T distortions become faster than the time scale of the neutrons (∼10^{-12} s) above T_{J-T}. This underscores the importance of including dynamics in any discussion of these systems.

The main results reported above for samples in the FMI regime are: 1) the functional relationship between changes in the non-thermal contributions to σ^2 (σ_{J-T/polaron}^2(T)) and the sample magnetization are the same as in the FMM regime; 2) The overall distortion that is removed as the sample becomes ferromagnetic at low T is significantly smaller for the FMI compared to the FMM, even for a rather small change in Ca concentration; and 3) A significant fraction of the sample (5-30% in this concentration range) remains unmagnetized and is still distorted at low T (4K) at B = 0.4T.

Point #1 suggests that the basic mechanism for FM behavior which involves the spins, the mobile charges, and the lattice, is the same in both the insulating and metallic FM regimes - thus the DE model (plus local distortions) is also the dominant coupling mechanism for most of the Mn sites at low Ca concentrations. Point #2 may at first be surprising but is consistent with the earlier extensive results reported by Downward et al. for samples in the CMR regime, namely that there is a large fraction of sites associated with the charge carriers that have a small distortion per Mn site. The small overall distortion removed for the x=0.16-0.2 samples is further evidence of this small distortion/site.

Point #3 may also be surprising - how does a small fraction of the sample consistently form an insulating layer between more conductive regions? It is perhaps less surprising if one first looks back at the LCMO CMR systems at partial magnetization. From our previous work, the turnover of the resistivity occurs when a significant magnetization has developed; up to that value of magnetization the resistivity is still increasing as T decreases (i.e. an insulator or semiconductor); also the turnover value of magnetization increases as the Ca concentration decreases. This behavior is comparable to the FM insulator sample with x = 0.16, except that turnover does not occur. The difference is that for the CMR sample the most distorted fraction of the sample does become magnetized at lower T - and the sample becomes conducting. For the FMI, much of this fraction remains distorted.
and never becomes magnetized at 0.4T. Thus the insulating and metallic systems are quite similar at partial magnetization.

It is useful here to comment further on the issue as to whether at 0.4T the sample is only partially magnetized or is fully magnetized but many domains are not aligned. Fig. 8 shows that at low M the first sites to be magnetized have a low distortion per site. We argue that these sites are related to the DE coupled FM clusters. If one argues that all sites are magnetized at 0.4T, then the data for the 16% sample in Fig. 8 should range up to \( \frac{M}{M_0} = 1.0 \) instead of 0.7; the break point would be near 0.75; then there would be an even larger fraction of easily magnetized sites with low distortions which would be inconsistent with the large number of filled \( e_g \) sites at low Ca concentrations. The only alternative would be to invoke a FM interaction that would lead to easily magnetized sites at low M that remain highly distorted (and thus have little distortion removed in the magnetized state). This seems unreasonable in view of the properties at slightly higher Ca concentrations.

In their dimeron model, Downward et al. suggested that the dimerons are preferentially located along filamentary clusters close to Ca sites; the argument is based on charge neutrality - the dimerons are + charged holes delocalized over two Mn sites while Ca on a La site acts like a negative charge. In such a model the chains of linked unit cells containing a Ca atom form pseudo-one-dimensional filaments within the insulating LaMnO\(_3\) host. Once the dimeron sites are magnetized as filamentary clusters, a further increase of magnetization requires magnetizing the surrounding J-T distorted Mn sites of the host lattice. Once enough of these sites are magnetized it will connect the filamentary chains and make the sample conducting; however the smaller the fraction of the sample that forms the filamentary structures, the larger the number of distorted Mn\(^{+3}\) \( (e_g) \) sites that would need to be magnetized (and be kept undistorted via charge hopping) before the filaments are connected and metallic conductivity can be achieved.

Note that these results again point to an intrinsic inhomogeneity of the material at the level of a few unit cells. One needs to consider nanoscale regions with quite different distortions, that change with the local magnetization - which in turn is determined by changes in T or B. These regions are determined by the distribution of dopants such as Ca, and also on the location of metal atom (Mn, La etc.) vacancies. It is likely that the poorly defined concentration at which the M/I occurs in LCMO is due to several connected effects – the distribution of Ca, correlations between the location of Ca sites and the location
of vacancies and the dynamics of the charge carriers. The NMR results mentioned in the introduction\textsuperscript{21} suggest that the low-distortion magnetic and high-distortion non-magnetic regions may be further subdivided into sites with different local B fields but the relative fraction of such sites is not clear.

Metallic conductivity through the CMR manganites in the FM phase is often considered to be a percolative problem but it is not simple percolation. If the holes had equal probabilities to be on any (Mn) site, then there would be uniform conductivity as is the case for low doping concentrations in n- and p-type semiconductors - and if such a manganite system were 50% magnetized, percolating magnetic clusters would exist across the sample and it would be metallic. Thus there must be preferred hole sites as discussed above. Considering only the Ca dopants, at 20 ±2 % Ca (the range for the metal/insulator transition) the system is well below the percolation limit for a cubic crystal (x = 0.31), and even at 25% - well into in the FM-metallic regime - the Ca atoms do not percolate; at these concentrations, chains of Ca atoms form many partially connected filaments but do not have connectivity across the sample. The electrical conductivity however depends on the available sites for the hole quasiparticles which will include Mn sites close to the Ca dopants. This expands the volume of the sample available for conduction to at least one unit cell about each Ca atom but still does not guarantee connectivity as the potentially conductive sites will be fluctuating. However if the fraction of conducting sites can be expanded beyond a unit cell (here by making more of the sample ferromagnetic via hole hopping), then these expanded filaments will eventually touch and connectivity can be achieved. For samples close to the metal/insulator transition (either for samples with x ≤ 0.2 at low T or for samples in the CMR regime which are only partially magnetized), the complex conductivity will depend sensitively on the conducting microstructure of the sample.

Finally we return to the nature of the Mn sites and the hole quasiparticles. In the introduction we pointed out that if the holes are hopping rapidly on a local scale there will be no Mn\textsuperscript{+4} sites on the time scales of most experiments, but there will be some Mn\textsuperscript{+3} sites if the holes have preferred locations and some Mn\textsuperscript{+3} sites are rarely visited by a hole. A large fraction of sites will be an average of occupancy by a hole and by an e\textsubscript{g} electron. A hole on a Mn site tends to reduce the local distortion as the J-T interaction is not present. When a hole moves off a site (and it now contains an e\textsubscript{g} electron) the site will begin to distort since the J-T interaction becomes active. Thus such sites will have some average distortion
depending on the hopping rate and the time scale of the measurement. EXAFS is a very fast probe \((10^{-15}\text{ s})\), much faster than phonon time scales, and will see a weighted average of all the distortions in the sample. Surprisingly the change in the local distortion is small for the first 50% of the sample that becomes magnetized for the CMR samples. This trend continues to be present in samples through the concentration driven transition from FMM to FMI \((x = 0.16-0.22)\). A crucial point is that the number of low distortion sites is far larger than the number of holes and involves approximately an equal numbers of electron sites. This approximate factor of two \((1.5-2.5)\) was the basis for Downward et al.\(^{14}\) to propose the dimeron model. However note that at any point in time Mn sites occupied by a hole will be in the process of becoming less distorted while the previously occupied site (which now has an \(e_g\) electron) will be increasing in distortion. Thus two sites are naturally involved. If the hopping is slow enough that the \(e_g\) sites become totally distorted before being revisited by a hole then there should be much larger distortions removed in the first 50% of magnetization. Alternatively if the hopping is very fast more than two sites may have a low distortion. The small decrease in distortion up to 50% magnetization is thus evidence for fast hopping on a local scale.

Alonso et al.\(^{15}\) also argue for localized Mn\(^{+4}\) sites and a reduce J-T distortion in the vicinity of Ca dopants, but do not provide a reason for the reduced distortion. The EXAFS confirm that there is a low distortion of many Mn sites - roughly two per Ca site. The number of Mn sites in the vicinity of the Ca atoms is more than 4x (note that there are 8 Mn neighbor sites per isolated Ca atom, but only 4 additional Mn neighbor sites for each Ca that is added to an existing linear chain of Ca) and thus the number of low distortion sites must be more restricted than only counting the number of closest Mn neighbors to Ca. If the hole can hop rapidly back and forth between two sites, it explains the low distortion per site removed for low magnetizations. If the model of Alonso et al. is slightly modified to correspond to partially delocalized holes in the vicinity of low J-T distortions (i.e. a hole localized over \(\sim 2\) Mn sites) instead of a completely localized Mn\(^{+4}\) hole site, then their model becomes identical to the dimeron model.

In summary, the new EXAFS data on LCMO samples with Ca concentrations near the metal-insulator transition \((x = 0.16-0.22)\) show similar behavior at the local scale as do the CMR samples at higher Ca concentrations. The distortions removed in the FM regime are small and show directly that there is a large fraction of low distortion Mn sites associated
with the charge carriers - the dimeron sites. A large fraction of the sample can be magnetized even though the sample is insulating - which is quite similar to the CMR systems at partial magnetization. The unmagnetized fraction is presumably highly distorted.

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