Universal Relationship between Magnetization and Changes in the Local Structure of La$_{1-x}$Ca$_x$MnO$_3$: Evidence for Magnetic Dimers

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We present extensive x-ray absorption fine structure measurements on La$_{1-x}$Ca$_x$MnO$_3$ as a function of the $B$ field (to 11 T) and Ca concentration, $x$ (21%–45%). These results reveal local structure changes (associated with polaron formation) that depend only on the magnetization for a given sample, irrespective of whether the magnetization is achieved through a decrease in temperature or an applied magnetic field. Furthermore, the relationship between local structure and magnetization depends on the hole doping. A model is proposed in which a filamentary magnetization initially develops via the aggregation of pairs of Mn atoms involving a hole and an electron site. These pairs have little distortion and it is likely that they form at temperature $T^*$ above $T_c$.

In recent years, the interest in manganites has grown significantly. They belong to a broader class of materials where charge-spin-lattice interactions play a crucial role in the observed properties. An understanding of these interactions in the manganites may provide insight into other strongly correlated electron systems, such as the high-$T_c$ superconductors.

Recently, Ramakrishnan et al. [9] have proposed a two band model of coexisting localized Jahn-Teller (JT) polaron and broadband states. The idea of phase separation in these materials is generally accepted; however, the microscopic details of how nanoscale clusters develop into a fully magnetized state is still poorly understood. Here we propose a mechanism in which Mn pairs form filamentary clusters which are interspersed with Jahn-Teller-distorted, nonmagnetic regions. This is consistent with Kumar et al [10], who have shown evidence for small clusters above $T_c$, where the magnetic susceptibility fits a Curie-Weiss law with a Curie constant nearly twice the expected value, suggesting Mn dimers. In addition, recent neutron scattering data [11] show a glasslike phase with short range order above $T_c$, which is also consistent with the Mn-dimer model presented here.

Previously, we have shown for a few samples [2,12] that the decrease in average local distortion, $\Delta(\sigma^2)$, as $T$ is decreased below $T_c$, is a simple function of the sample magnetization, $M$. Here $\sigma$ is the width of the Mn-O PDF obtained from extended XAFS (EXAFS), and $\Delta(\sigma^2)$ is the $T$- or $B$-induced change in $\sigma^2$. By extending those measurements to high fields (9–11 T) for some samples, and to a range of Ca concentrations, 0.21 $\leq x \leq 0.45$, we find that the plots of $\Delta(\sigma^2)$ versus $M$ (each normalized to their value at low $T$) depend primarily on hole concentration.

We find three important results for each sample: (i) slight distortion is removed until the fraction of magnetized sites ($M/M_0$) reaches $\sim 2y$, where $y$ is the hole concentration (ii) above $\sim 2y$, distortions are removed more rapidly as the sample becomes fully magnetized, and (iii) the point of change between these two behaviors occurs at $M/M_0 \sim 2y$. In addition, for the samples measured in an applied $B$ field, the above three results hold regardless of field, indicating that the change in local structure depends only on magnetization.

Transmission XAFS Mn K-edge data were collected on powdered samples at the Stanford Synchrotron Radiation Laboratory on beam lines 7–2, 10–2, and 6–2, using a Si(111) monochromator. The sample preparation has been described earlier [2] and accurate hole concentrations, $y$, were determined by iodometric titration with an uncertainty of $\pm 0.005$. For the XAFS samples, the pressed pellets were reground, passed through a 400-mesh sieve, and then brushed onto scotch tape which preferentially holds the smaller grains ($\leq 5 \mu m$) in a thin layer. Layers of tape were stacked to obtain a Mn K-edge absorption step height ($\mu_{Mn}$) $\sim 0.5$ for each sample. Generally, four scans were collected at each $T$ (and $B$ field) for each sample. For

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the $B$-field measurements, the field was aligned parallel to the tape layers such that the demagnetization factor is negligible. The magnetization data were collected on long rods with the $B$ field parallel to the axis; the demagnetization factor for this orientation is also negligible. The upper panel of Fig. 1 displays the magnetization at various magnetic fields for the 30% Ca sample; an applied $B$ field broadens the curve and shifts it to higher temperature.

In EXAFS analysis, the absorption $\mu_\rho$ from other atoms (preedge absorption) is removed first, then a sum of splines is used to obtain the background absorption $\mu_0$ above the edge [13,14]. Next the XAFS function, $\chi$, is obtained as a function of photoelectron wave vector from $\chi(k) = \mu/\mu_0 - 1$ (where $k = \sqrt{2me_0(E - E_0)/\hbar^2}$). See Fig. 2 of Ref. [2] for an example of the data quality. The $k\chi(k)$ data are then Fourier transformed (FT) to $r$ space. An expanded view of the first Mn-O $r$-space peak for La$_{0.7}$Ca$_{0.3}$MnO$_3$ for $T$ near $T_c$ at several fields is plotted in Fig. 1, bottom. As $B$ increases, the amplitude of the Mn-O peak increases; thus the average value of $\sigma$ must decrease, as observed (see Fig. 2, bottom). In contrast, for $T \ll T_c$ or $T \gg T_c$, no significant $B$-field induced change in $\sigma$ is observed. Similar $B$-field induced changes were observed for the 21% sample for $T$ near $T_c$. Changes in the Mn-O peak as a function of temperature also correlate with $T_c$ for all samples.

![Figure 1](image1.png)

**FIG. 1.** Top: Magnetization versus $T$ for La$_{0.7}$Ca$_{0.3}$MnO$_3$. Bottom: The $r$-space peak for the Mn-O bond (La$_{0.7}$Ca$_{0.3}$MnO$_3$) near $T_c \sim 260$ K. The fast oscillation is the real part of the transform ($FT_r$) while the envelope is $\pm \sqrt{FT_r^2 + FT_i^2}$, where $FT_i$ is the imaginary part. The FT range is 3.5–11.5 Å, with 0.3 Å$^{-1}$ Gaussian broadening.

The $r$-space data were fit [14] to similarly transformed standard functions, calculated using the FEFF6 code [15]. We used $E_0$ and $S_0^2$ determined in earlier studies [2], constrained the number of neighbors to 6, and fit the first Mn-O peak using an average bond length and a single broadening parameter $\sigma$ [16]. This method of fitting provides a single-parameter-measure of the local disorder for comparisons with $M$. For each temperature, separate fits were made to each of four traces and the average value of $\sigma$ calculated; the rms fluctuation about the average, gives the relative errors, which are comparable to the symbol size in most cases (See Fig. 2). The absolute error for $\sigma^2$ depends on the errors in $S_0^2$ and in the FEFF calculation (both systematic errors), and may be of order 10%–15%. This error primarily changes the static component of $\sigma^2$, and shifts the $\sigma^2$ versus $T$ plot vertically.

$\sigma^2(T/T_c)$ for the Mn-O peak is plotted in Fig. 2 for 30% and 45% Ca. For the 30% sample, the curves shift to higher $T$ and broaden as $B$ increases, as is also observed in the magnetization measurements (see Fig. 1, top).

The contributions to $\sigma^2(T)$ add up in quadrature when different broadening mechanisms are uncorrelated, i.e., $\sigma^2(T) = \sigma^2_{\text{phonons}}(T) + \sigma^2_{\text{static}} + \sigma^2_{\text{polaron}}(T)$, where $\sigma^2_{\text{phonons}}(T)$ is the contribution from thermal phonons, $\sigma^2_{\text{static}}$ arises from temperature independent static distortions, and $\sigma^2_{\text{polaron}}(T)$ is the contribution from the presence of hopping polarons, at 300 K (which we will argue below, are likely hopping “dimerons”). The latter becomes $T$.

![Figure 2](image2.png)

**FIG. 2.** $\sigma^2$ versus $T/T_c$ for the first Mn-O peak of La$_{0.55}$Ca$_{0.45}$MnO$_3$ ($T_c \sim 250$ K) and La$_{0.7}$Ca$_{0.3}$MnO$_3$ ($T_c \sim 260$ K). The dotted lines are guides to the eye. The solid line is the behavior if no polaron distortions are removed—i.e., $\sigma^2$ for CaMnO$_3$ plus a large static distortion. $\Delta(\sigma^2)$ is defined as the difference between this line and the experimental data.
independent when $M \sim 0$—we refer to this as $\sigma_{\text{RT-polaron}}^2$; the remaining weak $T$ dependence just above $T_c$ is nearly identical to that for pure CaMnO$_3$ [2] and arises from the thermal phonon contributions; the solid line in Fig. 2 is the sum of the phonon and RT-polaron distortion. The difference between this line and the data is $\Delta(\sigma^2(T))$ and represents the amount of polaron distortion removed (Fig. 2). Using $\Delta(\sigma^2(T))$ and $M(T)$, we can plot the changes in the local distortions as a function of $M$. In Fig. 3, we show $\Delta(\sigma^2)$ versus $M$, with each normalized to their low-$T$ values. The data follow the same linear relationship, within the errors, irrespective of whether the magnetization was obtained by a change in $T$ or $B$ (for $x = 0.3$ and $0.21$).

Thus, for a given sample, the distortion removed is a nearly universal function of $M$. An important feature of every plot is the low initial slope; little distortion is removed until the sample is more than 50% magnetized. Then $\Delta(\sigma^2(T))$ increases rapidly with $M$—i.e., $M$ and $\Delta(\sigma^2)$ are not quite in phase. The breakpoint occurs at $M/M_0 \sim 2y$ for each sample (see Fig. 4) [17], i.e., twice the number of holes. The breakpoint at $\sim 2y$ and the low slope for $M/M_0 < 2y$ suggests that the magnetization develops via pairs of Mn sites—a hole and a (distorted) electron site. We propose that such dimer pairs (which we call a dimeron) form at some temperature $T'$ [18] above $T_c$, which likely corresponds to the temperature at which there is a break in the susceptibility plots [10].

In this dimer model, an electron must be able to rapidly hop back and forth between two sites for the double exchange mechanism to be operative; this is only feasible for an electron-hole pair. For the JT distorted site it costs energy $E_{\text{JT}}$ to completely undistort the site; consequently, as long as holes are present, the least amount of energy is required when the magnetization develops in electron-hole pairs. The dimeron quasiparticle will also be mobile; the hole changes electron partners as it moves through the sample.

If we let the distortion per JT site be a constant, $\alpha$, then the maximum average distortion removed magnetized Mn site (for decreasing $T$ or increasing $B$ field) is only $\alpha/2$ in the initial stages of magnetization. Once the holes are used up, the distortion removed per Mn site would then increase to $\alpha$. This is qualitatively close to the behavior of the data shown in Fig. 3; however, the ratio of the slopes is closer to 1:4, instead of 1:2, as would be expected from this simple calculation. However for the dimeron, the electron is partially delocalized and the JT-like distortion will be reduced, although not eliminated. As a result, the ratio of the slopes would be larger than 1:2. For example, if the dimeron contains half the total polaron distortion of an electron-hole pair, then the distortion per site would be $\alpha/4$ and the ratio of slopes would be 1:4.

Another explanation for the large change in slope could be a variation in the size of the polaron distortions (different values of $E_{\text{JT}}$) throughout the system, due to strains and local variations in Ca content. The sites with the smallest distortion would then magnetize first. Since EXAFS gives

![Fig. 3](image_url) $\Delta(\sigma^2)$ versus relative magnetization for the five different concentrations. $\Delta(\sigma^2)$ and $M$ have been normalized to their respective values at low $T$. $\Delta(\sigma^2)$, defined in Fig. 2, is the decrease in $\sigma^2$ as $T$ is lowered below $T_c$ that is attributed to the loss of polaronic distortion. Note that the slope of $\Delta(\sigma^2)$ versus $M/M_0$ changes at roughly $M/M_0 \sim 2y$ (see Fig. 4).

![Fig. 4](image_url) Breakpoint in Fig. 3 versus hole concentration, $y$. The breakpoint occurs at $\sim 2y$ for each sample.
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16. Modeling with two Mn-O peaks (Ref. [3]) requires two amplitudes and two coupled $\sigma$'s, thus, a single parameter is not available for comparison to the magnetization.
17. La$_{0.79}$Ca$_{0.21}$MnO$_3$ may deviate since it is close to the metal-insulator boundary. See, Rivadulla et al., Phys. Rev. B 70, 172410 (2004). This sample also has a static distortion at low $T$, and is only 95% magnetized.
19. At this point, the electrons in the magnetic cluster are delocalized, but we keep pairs of (undistorted) open and gray circles for counting purposes.