Spin-lattice Correlations and Temperature Dependent Mn K-edge Structure in the La$_{1-x}$Ca$_x$MnO$_3$ Systems

F. Bridges, D. Cao and M. Anderson

Physics Dept. University of California, Santa Cruz CA, 95064 USA

Abstract. The La$_{1-x}$Ca$_x$MnO$_3$ system exhibits novel transport properties and unusual correlations between local distortions, magnetism, and the electronic structure. A large distortion, parameterized by the width of the pair distribution function, $\sigma$, develops as $T$ is increased through $T_c$ for values of $x$ roughly from 0.2-0.5 (the colossal magnetoresistance (CMR) regime); we associate this change of the local distortion with the formation of polarons. Changes in $\sigma$ as $T$ is reduced below $T_c$ depend on the magnetization, $M$, and can be described by the equation $\Delta \sigma = AM/M_0 + B$, where $A$ and $B$ are constants and $M_0$ is the saturation magnetization. Here we show that $\sigma$ is reduced when a magnetic field is applied and that the above equation holds even when the peak in the magnetoresistance occurs well below $T_c$. We also report on temperature dependent structure in the absorption edge, some of which again correlates with changes in the local structure.

INTRODUCTION

The substituted lanthanum manganites (La$_{1-x}$A$_x$MnO$_3$, where A is a divalent atom - Ca, Ba, Pb, etc) are excellent examples of systems in which there is a strong interplay between the electronic bands, magnetism and the local structure. As such they are important test cases for developing a better understanding of these interesting correlations. In this paper we report on several of these effects and outline some of the outstanding questions that need to be answered.

For $x$ roughly in the range 0.2-0.5, the La$_{1-x}$Ca$_x$MnO$_3$ systems exhibit a large magnetoresistance - hence the name colossal magnetoresistors (CMR). The spin-charge coupling is usually described in terms of the double exchange model (DE), originally proposed by Zenner [4], however, to explain the large magnitude of the magnetoresistance a significant electron-lattice coupling is also needed [5,6]. Experimentally, a large local distortion is observed in these materials; it develops as $T$ is increased through the ferromagnetic (FM) transition temperature, $T_c$, and is associated with the formation of small polarons [7-9]. The slightly increased lengths of some of the Mn-O bonds near and above $T_c$ appear to suppress the conductivity and thus enhance the magnetoresistance.

We have parameterized the local order/distortion by the width of the pair distribution function, $\sigma$, for each atom pair in the system [7,10]; here we focus mainly
on $\sigma$ for the Mn-O bond which we obtain from XAFS measurements. The different contributions to the broadening of the pair distribution function add in quadrature; i.e.

$$\sigma^2 = \sigma_{\text{static}}^2 + \sigma_{\text{phonons}}^2 + \sigma_{\text{polaron}}^2$$  \hspace{1cm} (1)

where $\sigma_{\text{static}}^2$ is any static contribution, $\sigma_{\text{phonons}}^2$ arises from lattice vibrations, and $\sigma_{\text{polaron}}^2$ is the distortion associated with polaron formation; it reaches its maximum value $\sigma^2_{\text{pm}}$ just above $T_c$.

In recent work [10] we have shown that there is a well defined relationship between changes in the local distortions and the sample magnetization, $M$. We first define the decrease in the polaron contribution (from its maximum value, $\sigma^2_{\text{pm}}$) by:

$$\Delta \sigma^2 = \sigma_{\text{static}}^2 + \sigma_{\text{phonons}}^2(T) + \sigma^2_{\text{pm}} - \sigma^2_{\text{data}}(T).$$  \hspace{1cm} (2)

Then the relationship between $\Delta \sigma^2$ and $M$ is given by:

$$\ln(\Delta \sigma^2) = AM / M_0 + B,$$  \hspace{1cm} (3)

where $A$ and $B$ are constants and $M_0$ is the saturation value of $M$. Note however, that each data point is at a different temperature. This relationship suggests that $\sigma^2$ should depend on the applied magnetic field. Here we show directly that the local structure changes when a magnetic field is applied at a fixed temperature near $T_c$. In addition we find that Eq. 3 persists even when the magnetic transition is broad or when the magnetoresistance peak-temperature, $T_{MR}$, occurs well below $T_c$, as is the case reported here for some co-doped samples containing Ca and Ti or Ga.

![Figure 1](https://example.com/figure1.png)

**FIGURE 1.** A plot of the difference $\sigma^2(B) - \sigma^2(0)$ with the magnetic field perpendicular (left) and parallel (right) to the X-ray polarization vector. From reference 11. The dotted lines indicate the $2\sigma$ error level.
In addition, the absorption edge structure provides information about the energy bands; the pre-edge structure provides constraints on parameters such as U and JH, while small features in the main edge also appear to reflect changes in the local structure.

MAGNETIC FIELD EFFECTS

The magnetic transition in the CMR systems moves to a slightly higher temperature with increasing applied magnetic field; consequently if $\sigma^2$ decreases with increasing magnetization as implied from earlier measurements, then it should also decrease when a static magnetic field, B, is applied at a fixed temperature near $T_c$. In Fig. 1 we plot the change in $\sigma^2 (\sigma^2(B) - \sigma^2(0))$ as a function of T for a 30% Ca sample. The difference has a maximum amplitude near $T_c = 260K$. The difference function can be roughly modeled as a rigid shift of the transition to higher T (solid line Fig. 1); however, since the FM transition broadens in a magnetic field, we have also included a broadening of the structural transition which changes the shape of the curve (See dot-dash line) and improves the quality of the fit [11]. Similar results are obtained for a 21% sample, with the peak in the difference occurring near 190K, just below the transition temperature of 210K. These results confirm that the local distortions are determined in part by the sample magnetization.

CO-DOPED SAMPLES

To further explore the changes in the local structure and the role of the Mn valence in these systems, we have co-doped several 30% Ca samples with Ti or Ga on the Mn site. Ti has a valence of +4 while Ga is +3; consequently adding these dopants should change the ratio of Mn$^{+4}$ to Mn$^{+3}$. However at relatively low concentrations (4-6%) these secondary dopants already play a significant role, with the peak in resistivity moving rapidly to lower temperatures; at 10% Ti there is no longer a metal/semiconductor transition and the sample is very resistive at low T. The effects for Ga are smaller.

The changes in the magnetic behavior are less pronounced. $T_c$ does decrease a little, but the two main effects are 1) the transition broadens and 2) the saturation magnetization decreases with increasing concentration, (down ~ 15% for Ga and 50 % for Ti at 10% concentration). Thus for these systems the metal/semiconductor transition at $T_{MS}$ and the magnetic transition at $T_c$ are decoupled. Consequently this provides an excellent test case for extending the investigation of correlations between $\sigma^2$, magnetization, and transport, to a new regime. For these systems we again find essentially the same relationship between $\Delta \sigma^2$ and M as given by Eq. 3, although there is a little curvature for $M/M_0 < 0.3$ because of the rounding of the transition (See Fig. 2). Note that the resistivity and magnetoresistance peaks occur in the top half of this magnetization range (i.e. for M roughly 70-90% of $M_0$), but there is no feature in Fig. 2 at the magnetization that corresponds to $T_{MS}$.
The physical basis for the above relationship is still not clear and there may be other functional forms that can also describe the data. We have therefore plotted lnΔσ² vs ln(1−T/T_c) to see if a power law in reduced temperature would model the data, but such plots yield strongly curved lines. The observed dependence of Δσ² on M clearly needs to be understood before a complete model can be developed for these systems.

Although there is no simple connection between Δσ² and transport we have found an unusual correlation: for a given co-dopant, the peak in resistivity occurs when σ₂ is reduced to a given value. When σ₂ does not reach this level as occurs for the 10% Ti sample, there is no resistivity peak. For the Ti doped samples, a lower value of σ₂ is required than for Ga, which suggests that Ti inhibits the electronic transport more than Ga. Further, there appears to be a trade-off between a static distortion that is not removed (at least not down to ~30K) and a polaron distortion that changes with T. At 300K, there is only a small difference in σ₂ for the different samples. The main difference in the temperature dependence of the different samples is primarily the amount of distortion that can be removed at low T. Thus the addition of the second dopant appears to introduce static distortions that impede charge transport, with the larger static distortions and higher resistivity occurring for Ti. A more detailed discussion will be given in a longer paper [12].

NEAR EDGE STRUCTURE

The Mn K-edge provides additional information and constraints on the electronic bands in these systems. Small changes in the edge and pre-edge correlate well with T_c, and the driving force again appears to be changes in the local structure about the Mn atom.

![FIGURE 2. A plot of lnΔσ² vs M/Mo for both the Ti and Ga doped samples. See Eq. 3.](image-url)
In Fig. 3 we plot the pre-edge structure for LaMnO$_3$ and the 30% Ca sample at several temperatures. There are two peaks, A$_1$ and A$_2$ for all of the substituted LaMnO$_3$ systems (also a third A$_3$, for high Ca concentrations), plus the peak labeled B. For the CMR systems, the amplitudes of the A$_1$ and A$_2$ change in opposite ways (A$_1$ increases while A$_2$ decreases) as the sample becomes magnetic, with most of the change occurring in a 60K range just below $T_c$. The A$_1$-A$_2$ splitting is small about 2.1 eV at 300K, and decreases about 0.4 eV in the FM state. Based on the calculations by Elfimov et al. [13] we attribute these peaks to weak dipole transitions made allowed by hybridization of the Mn 4p states with an odd symmetry combination of Mn 3d states ($e_g$) on neighboring Mn atoms [14]. To match the small splitting observed experimentally, Elfimov reduced U and $J_H$ to 4 eV and 0.7 eV respectively. These values indicate considerable covalency in this system. The reduction of the A$_1$-A$_2$ splitting in the magnetic state may indicate a further change in covalency.

The main edge has very little structure and shifts roughly uniformly with Ca concentration [9,10]. The lack of significant structure is at first surprising if the material is viewed as a mixture of ionic Mn$^{3+}$ and Mn$^{4+}$ sites. However the Mn 4p band is very broad (about 15 eV) and hence the 4p states are extended and will overlap with neighboring Mn atoms (a necessary condition for the hybridization described above). This partially explains the lack of significant structure in the edge; however, increased covalency likely also plays a role.

To investigate the structure more carefully, we have taken the difference between a data file at temperature $T$ and one at 300K which we use as a fiducial trace. To do so, the energy scale for each plot must first be corrected (to about 0.02 eV) using the reference data and carefully normalized above the edge. The resulting difference files for the 30% Ca sample are compared with those for the LaMnO$_3$ sample in Fig. 4; there is clearly a weak but reproducible temperature dependence. Here two aspects are clear – 1) the opposite dependencies of the amplitudes for A$_1$ and A$_2$ and 2) a new

![Figure 3](image-url)

**FIGURE 3.** A comparison of the pre-edge structure for 30% Ca with that of LaMnO$_3$ for several different temperatures.
structure for the 30% sample in the main edge (a dip/peak structure, see vertical lines on Fig. 4) that begins to be observed near Tc and grows rapidly just below Tc. The dip/peak structure has a separation of about 2 eV; we associate this splitting with the difference in the positions of the partial density of states (PDOS) for the Mn 4p_x (long Mn-O bond) and 4p_y,z (short Mn-O bond) states, as calculated by Elfimov et al. [13].

The Mn K-edge is a sum over all the Mn 4p states and thus will be a weighted sum over only two configurations, 4p_x and 4p_y,z, irrespective of any averaging caused by the extended nature of the 4p states. The short core hole lifetime will of course broaden the entire 4p PDOS. If one thinks in terms of valence (a mixture of Mn^{3+} and Mn^{4+}) and considers an average over only three Mn atoms as a result of the extended 4p states, then there will be a broad distribution of average charge which would not yield the observed structure. Thus we interpret the dip/peak structure in the difference data as arising from local distortions in the system. An extensive paper on the XANES will appear elsewhere [15].

CONCLUSIONS

We have shown that changes in the local structure are correlated with magnetism and transport in the substituted manganites and play an important role in determining their properties. First, the application of a magnetic field at Tc decreases the broadening of the Mn-O pair distribution function. This was anticipated from earlier experiments, but no model has yet been developed to understand this result in detail. On the experimental side, higher fields will be needed to determine the field dependence of this effect.

FIGURE 4. A comparison of the difference files for 30% Ca with that for LaMnO3. Note the scale - the absorption edge at the top has been multiplied by 0.03 to fit on this scale.
For a wide number of systems we have found that the decrease in the polaron contribution to $\sigma^2$, $\Delta\sigma^2$, is a linear function of $M$, even when the magnetoresistance peak occurs far below $T_c$ as occurs for co-doped samples containing Ca and Ti (Ga). Thus in these systems the local structure and magnetism appear more correlated than the local structure and charge transport. However there is some correlation between $\sigma^2$ and resistivity - the peak in the resistivity occurs when $\sigma^2$ has been reduced to a specific value, with a larger reduction required for Ti than for Ga. Neither of these results is understood in terms of a well defined model.

Finally the Mn pre-edge is temperature dependent as is a weak structure in the main $K$-edge. Both of these features are correlated with $T_c$ for CMR samples. It is likely that they are related to changes in the local structure but again a model is needed.

ACKNOWLEDGEMENTS

The experiments were performed at the Stanford Synchrotron Radiation Laboratory, which is operated by the U.S. Department of Energy, Division of Chemical Sciences, and by the NIH, Biomedical Resource Technology Program, Division of Research Resources. Some experiments were carried out on UC/National Laboratories PRT beam time. The work is supported in part by NSF grant DMR-97-05117.

REFERENCES