Spin-lattice Correlations and Temperature Dependent Mn *K*-edge Structure in the $La_{1-x}Ca_xMnO_3$ Systems

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Abstract. The $La_{1-x}Ca_xMnO_3$ 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, σ, 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 σ^2 as T is reduced below T_c depend on the magnetization, M, and can be described by the equation $\ln \Delta\sigma^2 = AM/M_o + B$, where A and B are constants and M_o is the saturation magnetization. Here we show that σ^2 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 ($La_{1-x}A_xMnO_3$, where A is a divalent atom - Ca, Ba, Pb, etc) are excellent examples of systems[1-3] 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 $La_{1-x}Ca_xMnO_3$ 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, σ, for each atom pair in the system [7,10]; here we focus mainly

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on σ 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.

$$\sigma^2 = \sigma^2_{static} + \sigma^2_{phonons} + \sigma^2_{polaron} \quad (1)$$

where σ^2_{static} is any static contribution, $\sigma^2_{phonons}$ arises from lattice vibrations, and $\sigma^2_{polaron}$ is the distortion associated with polaron formation; it reaches its maximum value σ^2_{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, σ^2_{pm}) by:

$$\Delta\sigma^2 = \sigma^2_{static} + \sigma^2_{phonons}(T) + \sigma^2_{pm} - \sigma^2_{data}(T). \quad (2)$$

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

$$\ln(\Delta\sigma^2) = AM / M_o + B, \quad (3)$$

where A and B are constants and M_o is the saturation value of M. Note however, that each data point is at a different temperature. This relationship suggests that σ^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.

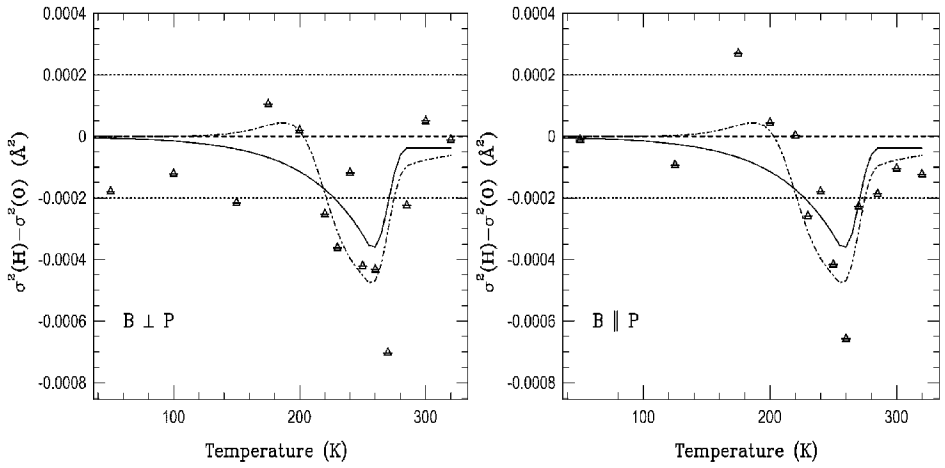

FIGURE 1. A plot of the difference σ^2(B)-σ^2(0) with the magnetic field perpendicular (left) and parallel (right) to the X-ray polarization vector. From reference 11. The dotted lines indicate the 2σ error level.

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In addition, the absorption edge structure provides information about the energy bands; the pre-edge structure provides constraints on parameters such as U and J_H, 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 σ^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 σ^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 σ^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 $M/M_o < 0.3$ 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_o), but there is no feature in Fig. 2 at the magnetization that corresponds to T_{MS}.

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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 $\ln\Delta\sigma^2$ 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 $\Delta\sigma^2$ on M clearly needs to be understood before a complete model can be developed for these systems.

Although there is no simple connection between $\Delta\sigma^2$ and transport we have found an unusual correlation: for a given co-dopant, the peak in resistivity occurs when σ^2 is reduced to a given value. When σ^2 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 σ^2 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 σ^2 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.

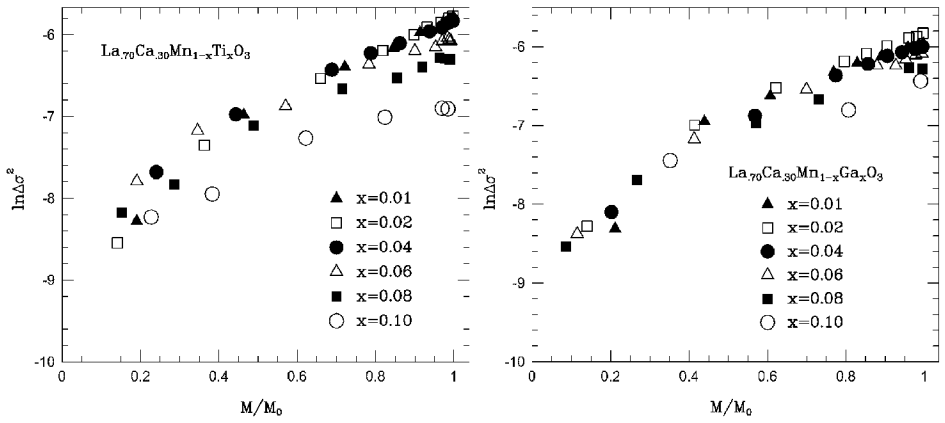

FIGURE 2. A plot of $\ln\Delta\sigma^2$ vs M/M_o for both the Ti and Ga doped samples. See Eq. 3.

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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

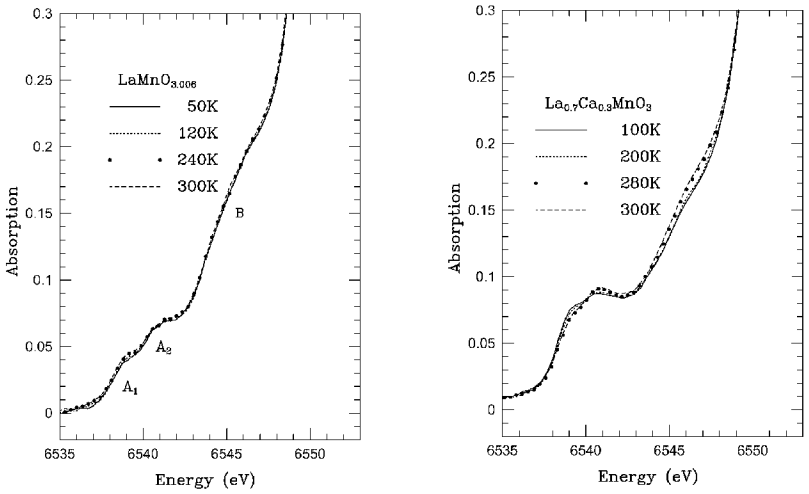

FIGURE 3. A comparison of the pre-edge structure for 30% Ca with that of $LaMnO_3$ for several different temperatures.

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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 T_c and grows rapidly just below T_c. 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 it *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 $p_{y,z}$, 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 T_c 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.

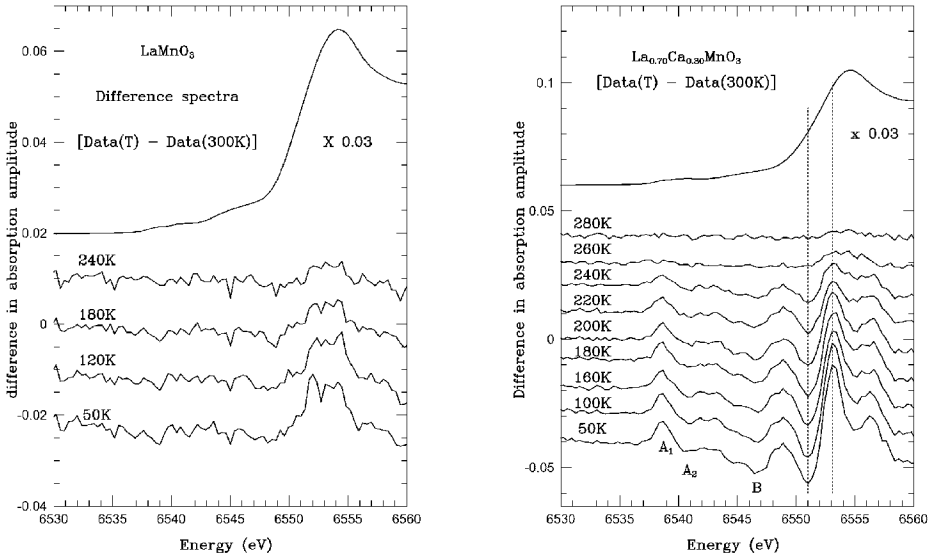

FIGURE 4. A comparison of the difference files for 30% Ca with that for $LaMnO_3$. Note the scale - the absorption edge at the top has been multiplied by 0.03 to fit on this scale.

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For a wide number of systems we have found that the decrease in the polaron contribution to σ^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 σ^2 and resistivity - the peak in the resistivity occurs when σ^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.

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