Temperature/magnetization-induced distortions in the local structure of substituted LaMnO₃

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Much of the work carried out on the Colossal Magnetoresistive (CMR) materials has been interpreted using the double exchange (DE) model which assumes Mn^{+3} and Mn^{+4} sites exist. In addition, to explain the large MR in films, it has recently been suggested that local distortions in the form of polarons, must also be present above the ferromagnetic transition temperature T_c; such distortions have now been observed. We present XAFS data which illustrate the magnitude of these distortions and show that the change in the Mn-O distortions correlates well with the magnetization. However the absorption edge is sharp and shows no structure indicative of two valence states, Mn^{+3} and Mn^{+4}, in either the polaron regime or in the charge-ordered material.
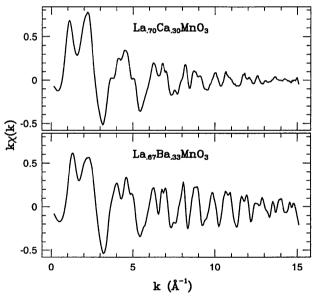**Keywords: CMR, XAFS, polarons.**

1. Introduction

Very large Magnetoresistive (MR) effects have been observed(Jin *et al.*, 1994) in thin film samples of the CMR materials, $R_{1-x}A_xMnO_3$ (R is a rare earth and A is Ca, Ba, Sr, Pb, etc.) near the ferromagnetic transition temperature, T_c. Shortly thereafter Millis *et al.*(Millis *et al.*, 1995) suggested that polaron-like local distortions must also be present to achieve the large MR values observed. They argued that although the Double Exchange (DE) model(Zener, 1951; Anderson & Hasegawa, 1955; de Gennes, 1960) used previously to describe these systems does produce a MR effect, it would be more than an order of magnitude smaller than the experimental observations. Local distortions above T_c would inhibit hopping of charge between Mn atoms thereby increasing the resistivity. Recent local structure studies using XAFS(Booth *et al.*, 1996; Subías *et al.*, 1997; Meneghini *et al.*, 1997; Booth *et al.*, 1998a; Subías *et al.*, 1998; Booth *et al.*, 1998b) and neutron pair distribution analysis(Billinge *et al.*, 1996; Louca *et al.*, 1997) have now shown convincingly that such local distortions do exist for the range of concentrations for which CMR is observed. Here we compare data for Ca and Ba substituted LaMnO₃.

The important concentration range for CMR is roughly $0.2<x<0.5$. In this range, the resistivity, ρ, increases rapidly as the temperature approaches T_c, (a metal-insulator (MI) transition) and then decreases slowly at higher temperatures. The resistivity over a range of temperatures

near T_c is decreased in a large magnetic field producing a large negative magnetoresistance.(Jin *et al.*, 1994) At higher dopant concentrations these materials are antiferromagnetic insulators with charge ordering (CO) at low temperatures.(Ramirez *et al.*, 1996)

Most of the models used to describe these systems are based on the idea that in the substituted manganites, there is a mixture of Mn^{+3} and Mn^{+4} ions based on composition. The isolated Mn^{+3} ion is a Jahn-Teller (J-T) ion and has a local distortion while the Mn^{+4} ion is symmetric. However in the high concentration regime the nature of the defect structure is less clear. Mn^{+3} has an extra electron in an e_g state with its spin parallel to the local Mn moment formed of t_{2g}^3 electrons.(Hund-rule coupling). In the metallic FM state, holes in the e_g band moves freely through the crystal, hopping from one Mn (or O) to the next(Zener, 1951; Anderson & Hasegawa, 1955; de Gennes, 1960) and the quasiparticle is called a large polaron. Hopping is enhanced when two neighboring Mn moments are parallel in the FM state, but suppressed when the local moments are not parallel (costs energy to flip the e_g spin). If the hopping is slow enough the lattice distorts, a small polaron forms (roughly a unit cell) and the resistivity increases. In the presence of a magnetic field the spins remain aligned to higher temperatures which lowers the resistivity near T_c.

Figure 1
The k-space data for LaMnO₃ substituted with 30 % Ca and 33 % Ba.

For polaron-like distortions to develop in the paramagnetic phase requires that charge be localized on either the Mn or O atoms for times comparable or longer than the optical phonon period. The X-ray absorption edge is sensitive to the local Mn electron configuration, and should show an inflection point and a broader edge if Mn^{+3} and Mn^{+4} are present. Such is not the case; the edge is sharper than expected (See Sec. 3.).

2. Experiments

XAFS data were collected at the Mn K-edge using fine (10 μm) powdered samples on tape of $La_{1-x}Ca_xMnO_3$ and

$La_{1-x}Ba_xMnO_3$. The data were collected at SSRL on beamlines 2-3 (Si (220)) and 10-2 (Si (111)). The slit height was 0.7 mm, and a Mn foil reference was used to calibrate the energy of the monochromator on each scan. For additional experimental details see (Booth *et al.*, 1998a; Booth *et al.*, 1998b).
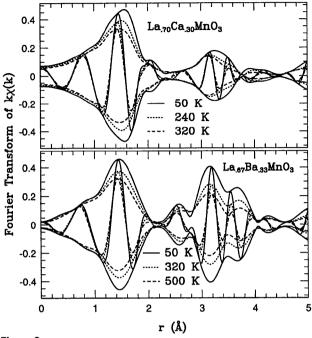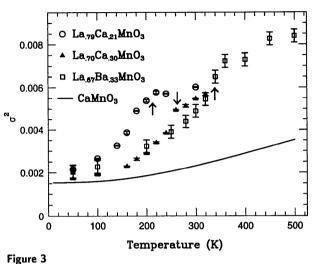

Figure 2

The FT of $k\chi(k)$ for the Ca and Ba substituted samples. The FT ranges are: 3.5-14.5 Å^{-1} for Ca and 3.3-10.5 Å^{-1} for Ba, both with a 0.3 Å^{-1} Gaussian broadening.

Fig. 1 shows the k-space data for Ca and Ba substituted samples at T = 50K. Fig. 2 compares the Fourier transform (FT) of the XAFS oscillations for two CMR samples at several temperatures. For both samples there is a strong decrease in the Mn-O peak amplitude with temperature. In contrast, there is very little change of the Mn-O peak with T for non-CMR samples (not shown).
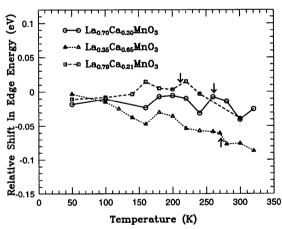
To quantify this change, σ is determined in detailed fits. In Fig. 3 we plot σ^2 vs temperature for two Ca-doped, the Ba-doped, and a $CaMnO_3$ reference sample. Three or four traces were collected at each temperature (except for Ba) and analyzed independently. The relative errors shown give the rms variation of the average of the fit results at each temperature. The low value and the weak temperature dependence of σ^2 for $CaMnO_3$ is typical of a Debye solid with an ordered O environment and stiff Mn-O bonds. In contrast, the data for the other samples increase considerably at low T and show a step in σ^2, which levels out near T_c for each sample. We interpret the step in σ^2 as evidence for polaron formation.

The main Mn edge in these materials is sharp ($\sim$6eV)(Booth *et al.*, 1998b) - sharper than observed in other Mn-oxides ($\sim$10-12 eV).(Manceau *et al.*, 1992) The average edge shifts to higher energy with Ca substitution, and is about 3 eV higher for $CaMnO_3$ (Mn^{+4}) than for $LaMnO_3$ (Mn^{+3}). However the edge for the substituted samples is not a simple composition-weighted combination of the edges for $LaMnO_3$ and $CaMnO_3$; it is steeper than expected from

such a model. In addition, there is no change in edge position at temperatures where polaron-like distortions form nor in the charge-ordered regime in which the Mn^{+3} and Mn^{+4} are thought to be spatially ordered. This raises the question - - where does charge localization occur? on Mn or O?

Figure 3

A plot of σ^2 vs temperature for $CaMnO_3$, 21 and 30 % Ca and 33% Ba substitution. Arrows show T_c.

Figure 4

Relative shift in edge position as a function of T for 21, 30, and 65 % Ca. Each edge position is obtained by fitting to the 50K data and determining the net shift. The 65 % Ca is CO. Relative errors are $\pm$ 0.02 eV. Arrows show T_c or T_{CO}.

The edge position is often determined from the derivative peak: however for these samples the derivative peak is broad and the inflection point on the edge moves relative to the half-height energy as the composition is changed. Consequently the average edge position cannot be measured accurately this way. Since the overall shape changes little from $LaMnO_3$ to $CaMnO_3$, the average shift as a function of concentration can be obtained by fitting all edges to either the $LaMnO_3$ or $CaMnO_3$ edge; temperature changes can be determined by fitting the 50K data to all the higher temperature edges. Fig. 4 shows that the average edge position changes very little with T, with no change at T_c or T_{CO} (arrows).

3. Discussion and Conclusions

XAFS studies of bulk CMR powders show that they have small local distortions at low temperatures, approaching that for $CaMnO_3$, while above T_c, the local structure becomes distorted. This correlates qualitatively with the resistivity - - the Mn-O distortions are small when the the resistivity is low.
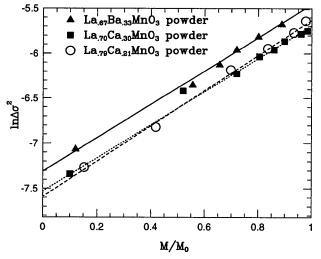

Figure 5

A plot of $\Delta\sigma^2$ vs normalized magnetization for powder samples substituted with Ca and Ba. In each case the graph is a straight line.

The data also suggest that the shape of the step change in σ^2 is dependent on the sample magnetization. We fit the data above T_c to a Debye model (σ_D^2) plus static distortion and extended the results to lower temperatures. The contribution to σ^2 attributed to polarons, σ_{FP}^2, is determined as the difference between σ_D^2 and the data, σ_{data}^2, at the lowest temperature. The decrease in disorder as the temperature is lowered is given by

$$\Delta\sigma^2(T) = (\sigma_D^2(T) + \sigma_{FP}^2) - \sigma_{data}^2(T). \quad (1)$$

In Fig. 5, $\ln(\Delta\sigma^2)$ is plotted as a function of the magnetization, M, for Ca and Ba (using M vs T data). Each plot is a straight line, even though the steepness of the magnetic transition is not the same for all samples. This indicates that a clear relationship exists between local structure and magnetism for both dopants, but the exact nature of this coupling is still not known Finally, the X-ray absorption edge is surprisingly sharp(Booth et al., 1998b) in view of the assumption of distinct Mn^{+3} and Mn^{+4} sites. If the localization of the e_g electrons on Mn^{+3} changes, there should be a small edge shift but experimentally it is less than ±0.03 eV from 50-320K for CMR samples (Fig. 4). These and other(Subías et al., 1997) edge studies indicate that all Mn atoms have an average valence. Thus it is difficult to reconcile the sharp absorption edge at all temperatures with the

clear structural change near T_c, under the assumption that the hole or electron is localized primarily on the Mn atoms.

Several variations of the model can be made to address this deficiency. The holes may be localized more on the O atoms or in the Mn-O bond above T_c. Since the holes are induced by the presence of a Ca^{+2} ion, possibly the hole is spread over the twelve nearest neighbor O atoms to the Ca but the localization changes below T_c.

Another possibility is that the smallest unit is not a single hole or electron polaron, but a small cluster or domain within which the electron motion is rapid. All Mn atoms would have the same average electron density. The distortions would then be associated with the domain boundaries, with many boundaries above T_c, and few at low T where the sample is fully magnetized.

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