Changes of the local distortions and Colossal magnetoresistive properties of $La_{.7}Ca_{.3}MnO_3$ induced by Ti or Ga defects

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Abstract

The magnetoresistive properties of $La_{0.7}Ca_{0.3}MnO_3$ change rapidly when Ti or Ga are substituted on the Mn site for concentrations, x, from 1 to 10%. The samples exhibit colossal magnetoresistance (CMR) and the resistivity increases dramatically with dopant concentration. The temperature of the resistivity peak, T_R, shifts rapidly to lower temperatures with increasing x and the ferromagnetic transition broadens. However, the transition temperature, T_c, is only slightly suppressed. Consequently T_R occurs well below T_c for x above 2%. Investigations of these materials using Mn XAFS show that changes in the local structure, parameterized by the pair-distribution width, σ, correlate well with T_c and the sample magnetization. For a given dopant, the resistivity peak occurs when σ^2 decreases below a critical value. Both dopants produce extended defects which increases the resistivity of the nearby material considerably. The data suggest that even at $\sim 4\%$ most of the sites are slightly distorted at low T.

The series of substituted manganites, $La_{1-x}Ca_xMnO_3$, are colossal magnetoresistors for x roughly in the range 0.2-0.5[1–3]. A theoretical description of these systems that has emerged recently is a combination of the double exchange (DE) model[4] and a lattice distortion that forms[5] as the temperature, T, is raised through the ferromagnetic (FM) transition temperature, T_c. The local distortions are attributed to the formation of polarons near and above T_c. Below T_c, the distortions disappear, the resistivity drops, and the system becomes metallic.

The DE model is usually considered in terms of a mixture of Mn^{+3} and Mn^{+4} ions which results from the substitution of Ca for La; each Ca produces an Mn^{+4} site. Each Mn^{+3} site contribute an electron to the e_g band and for 30% Ca, the lower e_g is 70% full. The spin of each e_g electron is Hund-rule coupled to a local Mn moment and if the moments are aligned as in the FM state, the e_g electrons hop rapidly from one Mn site to another on time scales faster than phonon frequencies – the lattice cannot respond and is well ordered. Above T_c the Mn moments are no longer aligned, the e_g electrons hop more slowly (it now costs energy to hop as the spin must flip) and are localized long enough on a given site for the lattice to respond. The O atoms then move in response to localized charge, leading to a distribution of long and short Mn-O bonds. These distortions have been observed both in XAFS[6–8] and in pair distribution analysis of neutron data[9,10].

To explore the importance of having +3 and +4 Mn sites, we introduce a second dopant on the Mn site; Ti^{+4} or Ga^{+3}. Eliminating some of the Mn^{+4} by adding Ti should be similar to reducing the Ca concentration. Adding Ga should have a smaller effect as most of the Mn sites are +3 and this substitution does not affect the number of Mn^{+4}.

Surprisingly, both dopants have a large effect on the transport properties, even at concentrations of a few percent. The resistivity increases rapidly with concentration and the temperature of the resistivity peak, T_R, shifts rapidly to lower temperatures as shown in Fig. 1 for Ti. In contrast, T_c is only slightly suppressed, the transition is broadened, and the saturation magnetization at low temperatures is reduced by roughly two at 10% concentrations.

The local structure is monitored by using XAFS to obtain the width of the Mn-O pair distribution function, σ. For these materials there are three contributions to the width - thermal fluctuations (phonons), σ_{th}; static disorder, σ_{st}; and dynamic distortions attributed to polarons, σ_{pol}. These quantities add in quadrature to give total value, σ^2_{tot}.

In Fig. 2 σ^2_{tot} is plotted as a function of temperature for several Ti concentrations. The rapid increase with T for most samples below roughly 250K is attributed to the formation of polarons[6,7] and the break point where the temperature dependence becomes slower, occurs very close to T_c. As the concentration of either Ti or Ga is increased, the polaron contribution decreases and the static contribution (observed at low temperatures) increases. Yet the sum of these contributions is nearly constant as if some of the polaron-induced distortion is frozen by the defect. In all cases that a polaron contribution can be extracted, we find that the same relationship between changes in σ^2(T) and magnetization, M, as observed previously[7]. The resistivity peak occurs at various values of M from 0.75-0.9M_o (M_o is the low T value), but there is no anomaly in σ^2 at T_R. However, as σ^2 decreases with T, we find that it must reach a critical value before a resistivity will peak form. At the resistivity peak, the value of $sigma^2_{crit}$ is approximately 0.0029 Å^2 for Ti-doped sample; for Ga, σ^2_{crit} = 0.0033 Å.

It is not clear why a critical value for σ^2 should exist as many different changes in the distribution of local distortions could lead to a comparable net decrease in σ^2 (note that σ^2 is an average over sample volume). In our earlier work we used a 2-fluid model with a (T-dependent) fraction of the sites ordered and the rest disordered (polaron disorder). For the present samples with substitution on the Mn site, it is likely that few of the sites become well ordered; instead there is likely a distribution of partially ordered sites plus the strongly disordered sites when a polaron is present. Note that the resistivity is strongly dependent on the local bond lengths; a slight lengthening significantly decreases the orbital overlaps. Consequently if the situation were described by only ordered and disordered sites, then the resistivity of two samples would be comparable when σ^2 is the same (that is not observed experimentally). However, for sites that only partially order at low temperatures, the material will be much more resistive even when a large fraction of the sample is in this

"ordered" state at low T, in qualitatively agreement with the data.

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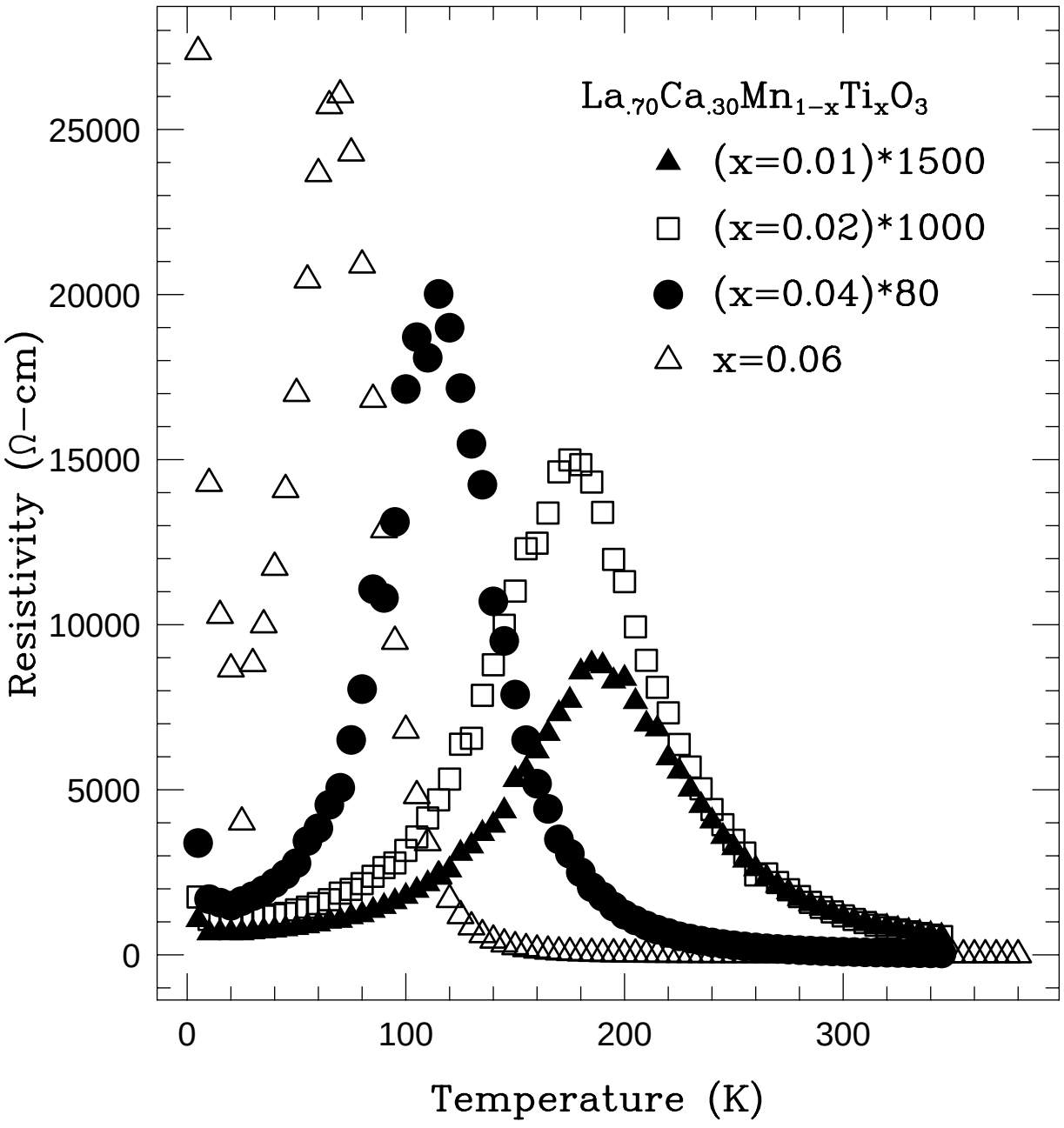
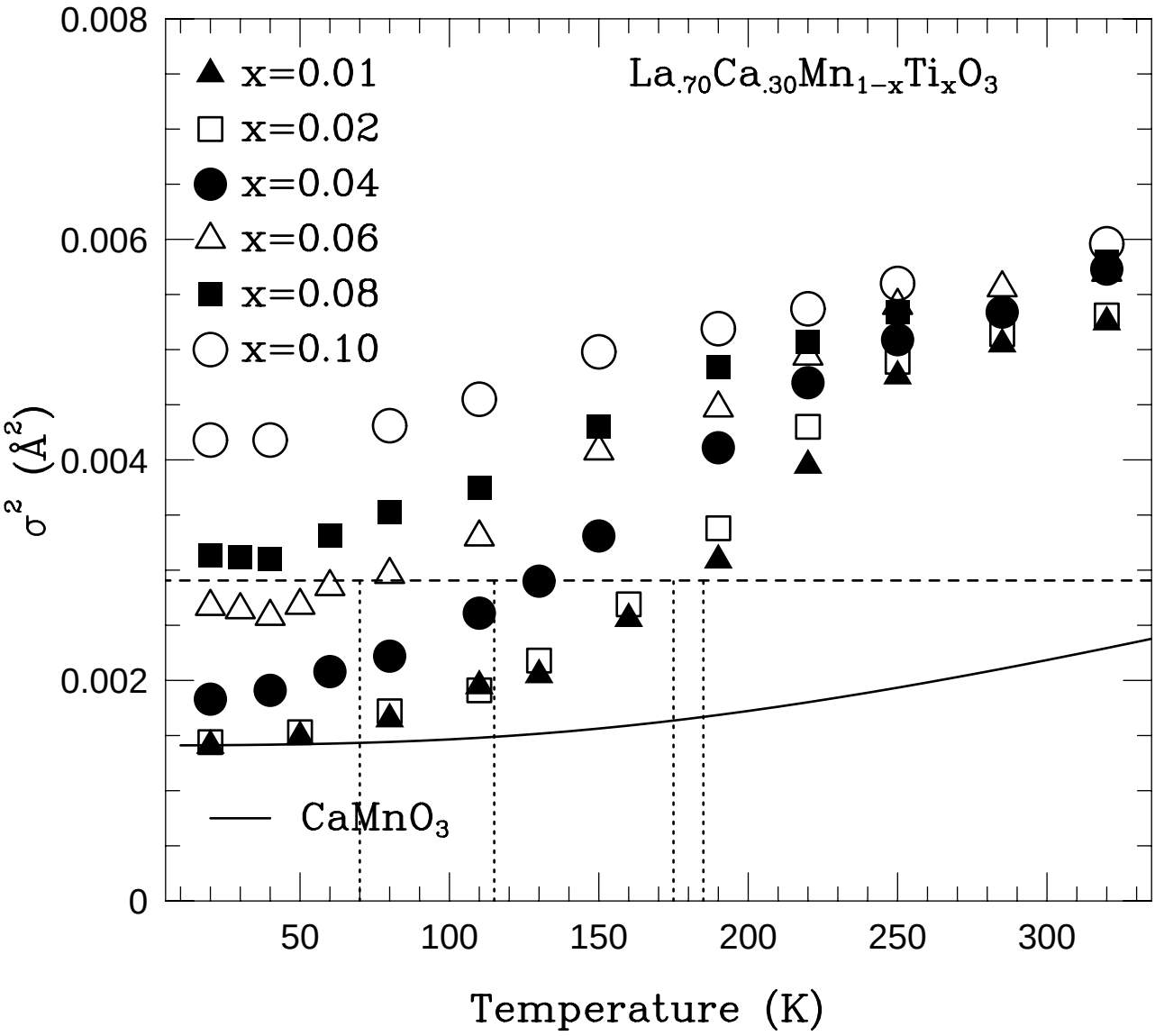
FIGURES

FIG. 1. The resistivity as a function of temperature for the Ti substituted samples.

FIG. 2. σ^2 as a function of temperature for the Ti substituted samples. The vertical lines are the positions of the resistivity peaks for (from left to right) x = 0.06, 0.04, 0.02, and 0.01; they cross the data close to $\sigma^2 = .0029$ Å^2.


La.70Ca.30Mn1−xTixO3
(x=0.01)*1500
(x=0.02)*1000
(x=0.04)*80
x=0.06
Resistivity (Ω−cm)
25000
20000
15000
10000
5000
0
0
100
200
300
Temperature (K)


0.008
0.006
0.004
0.002
0
σ² (Å²)
x=0.01
x=0.02
x=0.04
x=0.06
x=0.08
x=0.10
La.70Ca.30Mn1−xTixO3
CaMnO3
50
100
150
200
250
300
Temperature (K)