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THE STATIC AND DYNAMIC LATTICE EFFECTS IN  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ P. Dai,<sup>a</sup> Jiandi Zhang,<sup>a,b</sup> H.A. Mook,<sup>a</sup> F. Foong,<sup>c</sup> S.-H. Liou,<sup>c</sup> P.A. Dowben<sup>c</sup> and E.W. Plummer<sup>a,b</sup><sup>a</sup> Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, U.S.A.<sup>b</sup> Department of Physics, University of Tennessee, Knoxville, Tennessee 37996, U.S.A.<sup>c</sup> Department of Physics, University of Nebraska, Lincoln, Nebraska 68588-0111, U.S.A.

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The structural and magnetic behavior of the perovskite insulator  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  were studied as a function of temperature from 15 to 300 K by neutron powder diffraction. Although this compound shows an anomalous response of the lattice parameters around  $T_c$  (150 K), the behavior of the oxygen/manganese Debye-Waller factors is in clear contrast to its “colossal magnetoresistance” (CMR) counterpart  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ . We speculate that the difference is intimately associated with the metal-insulator transition in the latter compound. Copyright © 1996 Elsevier Science Ltd

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The recent rediscovery of “colossal magnetoresistance” (CMR) in perovskite-based  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $A = \text{Ca}, \text{Sr}, \text{Ba}$ ) [1] has generated considerable interest in these materials. For the electronic hole doping concentration of  $x \sim 1/3$ , these compounds exhibit an insulator-to-metal transition that is intimately related to the paramagnetic to ferromagnetic ordering. For lower doping concentrations ( $x \leq 0.2$ ) the high-temperature ( $T$ ) phase is paramagnetic and the low- $T$  phase can be antiferromagnetic (AF), canted antiferromagnetic (CAF), or ferromagnetic, but the resistivity shows insulator behavior at all temperatures. The concept of “double exchange” (D-E), developed some 40 years ago [2], has been long known to carry the essential physics of the magnetic interactions [3] between the Mn ions which have either a trivalent ( $\text{Mn}^{3+}$ ) or tetravalent ( $\text{Mn}^{4+}$ ) state due to the substitution of a trivalent La ion by a divalent alkaline-earth ion. However, recent theories [4–6] suggest that double exchange alone cannot account for the large resistivity drop below the paramagnetic to ferromagnetic phase transition temperature  $T_c$ . A strong electron-phonon coupling, due directly to the dynamic Jahn-Teller (J-T) type distortions of the oxygen octahedra around  $\text{Mn}^{3+}$ , must also play an essential role [5,6]. The physical picture, according to

Millis *et al.* [5], is as follows. The  $\text{Mn}^{3+}$  in the parent compound  $\text{LaMnO}_3$  is a static J-T ion [7]. Doping the system with a divalent ion would gradually destroy the static and replace it with slowly fluctuating (dynamic) local J-T distortions that could trap the conduction band electrons as polarons. The polaron effect would compete with the D-E mechanism. For  $0.2 \leq x \leq 0.5$ , the D-E mechanism dominates the electronic behavior at low- $T$  (metal) while the polaron effect is important for  $T$  above  $T_c$  (insulator). As a consequence, the oxygen Debye-Waller factors should have a sudden drop below  $T_c$  so that it creates a discontinuity (*kink*) at  $T_c$  in the *rms* motion amplitudes of the oxygen atoms.

Shraiman [8] has characterized this *kink* in the oxygen *rms* motion at  $T_c$  as the “smoking gun” of their dynamic J-T theory [4,5]. Recent neutron diffraction studies by Dai *et al.* [9], Radaelli *et al.* [10], and Caignaert *et al.* [11] on the CMR  $B_{0.7}A_{0.3}\text{MnO}_3$  ( $B = \text{La}, \text{Pr} \dots; A = \text{Ca}$ ) system show a clear discontinuity in the *rms* motion of the oxygen atoms, consistent with the theoretical prediction. However, earlier neutron diffraction experiments on  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , which has a metal-to-metal transition, by Martin *et al.* [12] have shown no anomalous behavior in the *rms* motion of the oxygen atoms near  $T_c$ . We have investigated the static and dynamic properties of the  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ ,

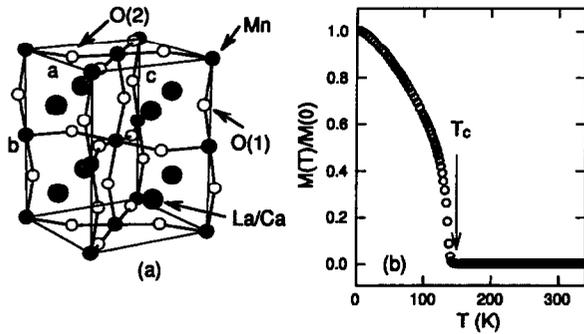


Fig. 1. (a) The schematic crystal unit cell. The positions of La/Ca, Mn, O(1), and O(2) atoms and the lattice parameters for  $a$ ,  $b$ , and  $c$  directions of the orthorhombic cell are clearly labeled. (b) Sample bulk magnetization as a function of temperature in arbitrary units.

which has an insulator-to-insulator transition, in this study in an attempt to understand the difference reported in the literature.

Our neutron experiments were performed using the HB-1A triple-axis and HB-4 high-resolution powder diffractometers at the High-Flux Isotope Reactor at Oak Ridge National Laboratory as described before [9]. Figure 1(a) shows the crystal structure of this compound, which is an orthorhombic ( $Pnma$ ) structure both above and below  $T_c$ , the same as observed for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $0.2 \leq x \leq 0.5$ ) [13]. Figure 1(b) is the measured bulk magnetization. The paramagnetic to ferromagnetic phase transition with  $T_c = 150$  K is clearly evident in the data, consistent with the established phase diagram for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  [14, 15]. The sample is insulating throughout the measured temperature range, however, there is a weak feature in the resistivity [16, 17] around  $T_c$  suggesting a possible correlation between transport and magnetism in this system. Recent neutron diffraction results by Kawano *et al.* [18] for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  show that the magnetic structure in the insulating part of the phase diagram is always a CAF at low temperatures. No evidence for such behavior was found in our insulating  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  sample although the possibility of a small canted moment beyond the sensitivity of the measurements cannot be ruled out. However, since the goal of the experiment is to test whether the nonmagnetic structure parameters have anomalous behavior, we will simply regard the compound as a pure ferromagnet below  $T_c$ .

Figure 2 summarizes the  $T$  dependence of the lattice parameters [ $a$ ,  $b$ , and  $c$  from Fig. 1(a)]. The data for the  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  compound is displayed with the open circles referenced to the left vertical axis. Our previous measurements for the  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$  are

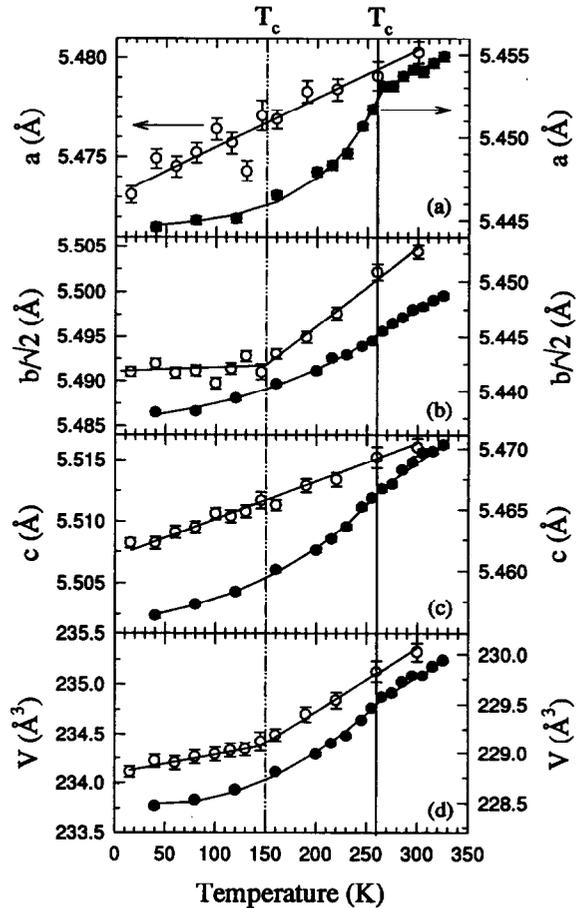


Fig. 2. Lattice parameters as a function of temperature for  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  ( $\circ$ ) and  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$  ( $\bullet$ ) in (a)  $a$ , (b)  $b$ , and (c)  $c$  directions. (d) shows the cell volume as a function of temperature. The paramagnetic to ferromagnetic phase transitions are marked by dot-dashed and solid vertical lines for  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  and  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ , respectively. Solid lines result from fitting procedures described in the text.

plotted as solid circles referenced to the right-hand scale. Note that there is an abrupt change in the temperature dependence of the volume expansion at  $T_c$  [see Fig. 2(d)]. Fitting the data with a linear expansion in  $T$  yields  $V = 234.1 + 2.06 \times 10^{-3}T$  ( $\text{\AA}^3$ ) for  $T < T_c$  and  $V = 233.55 + 5.94 \times 10^{-3}T$  for  $T > T_c$ . This gives a change in the thermal expansion coefficient of  $3.88 \times 10^{-3} \text{\AA}^3/\text{K}$ , or almost 200%, around  $T_c$ . The top three panels show the temperature dependence of the lattice parameters in the three different directions. If we assume that  $a$ - $c$  axes form the basal plane, it is clear that the crystal is expanding with  $T$  by only increasing the lattice parameters in the basal plane and 95% of the volume expansion is accounted for by the in-plane thermal expansion below  $T_c$ . Above  $T_c$ , however, the abrupt change in the volume expansion coefficient is

totally a consequence of the inter-plane lattice expansion. Therefore, we speculate that the ferromagnetic to paramagnetic transition at  $T_c$  is intimately associated with the electron coupling between planes, most likely the result of the Mn-Mn interaction along the  $b$ -axis.

Before comparing the  $T$ -dependence of the lattice parameters of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  with  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ , we consider the dynamic motion of the individual atoms, analyzed using the same method as before [9], and shown in Figs. 3 and 4. Both figures have the same format as Fig. 2, in that the data for the  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  is shown with open circles and the data for the  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$  is plotted as solid circles. The first significant observation is that there is no *kink* or inflexion in the *rms* motion for any of the atoms in the  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  compound around  $T_c$ , in clear contrast to its CMR counterpart. Therefore we conclude, from our data on  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  and previous results on  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  [12], that there is no sudden change in the *rms* motion of the oxygen atoms at  $T_c$  that do not exhibit a metal-insulator transition.

We now return to Fig. 2 and ask what one might expect for the *rms* motion of the oxygen atoms in and between the basal planes [O(2) and O(1), respectively]. Since the enhanced thermal expansion coefficient above  $T_c$  is a direct consequence of the interplanar lattice expansion, one would expect anomalous behavior in the *rms* motion of O(1). However, Fig. 3(a) shows that the *rms* motion of the O(1) atoms in the insulating phase of the  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  compound extrapolates exactly to the *rms* motion in the insulating phase of the  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$  compound. Figure 4(a) shows that this behavior is also manifested in the motion of the Mn atoms. The anomalous behavior is in the in-plane oxygen atoms [O(2)]. The *rms* motion in the  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  compound is appreciably higher than in the insulating ( $T > T_c$ ) phase of the  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$  compound [19], even though the in-plane thermal expansion coefficient [Fig. 2(a) and (c)] seems to be the same in the insulating phase of both crystals, i.e.  $T > 260$  K.

The behavior of the lattice parameters for the metal-insulator transition in  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$  is quite different than that of the insulator-insulator transition compound  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ . First, the metal-insulator transition is a gradual type transition in metallicity ranging from nearly 80 K below  $T_c$  up to  $T_c$ , that can be clearly seen in the bulk transport data such as resistivity [1, 13, 14]. Comparing the thermal expansion below and above this transition region ( $T < 150$  K or  $T > 260$  K), we find that the volume expansion coefficient [ $V(T) = V_0 + \alpha T$ ] in the 35% Ca-doped compound is

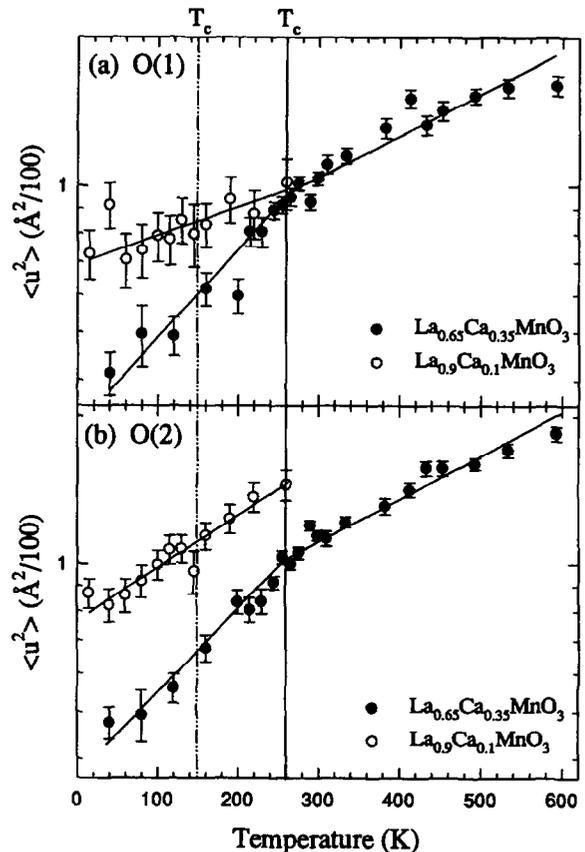


Fig. 3. Isotropic Debye-Waller factors vs  $T$  as obtained from Rietveld refinements for (a) O(1), (b) O(2). Paramagnetic to ferromagnetic transition temperatures of both compounds are clearly marked. The data is plotted on a semi-log plot which seems to give a better representation of the changes as a function of temperature than a linear plot. Solid lines are guides to the eye.

very similar to that in the 10% Ca-doped sample. For example, the 35% compound has  $\alpha = 2.8 \times 10^{-3} \text{ \AA}^3/\text{K}$  for  $T < 150$  K and  $\alpha = 5.78 \times 10^{-3} \text{ \AA}^3/\text{K}$  for  $T > 260$  K. These values are very close to that of the 10% compound. However, the change in volume expansion coefficient in the 35% Ca-doped sample is very different in origin than that for the 10% sample. As we have already discussed, the change in the thermal expansion for the 10% sample is due almost entirely to the change in thermal expansion between the planes while for the 35% sample the change is a consequence of the in-plane lattice expansion.

So far all of the existing data for the manganites that exhibit a metal-insulator transition show an anomalous behavior in the oxygen *rms* motion near  $T_c$ , consistent with the theory of Millis *et al.* [5]. In the low doping concentration regimes ( $x \leq 0.2$ ), there are two qualitative predictions from the theory that can be

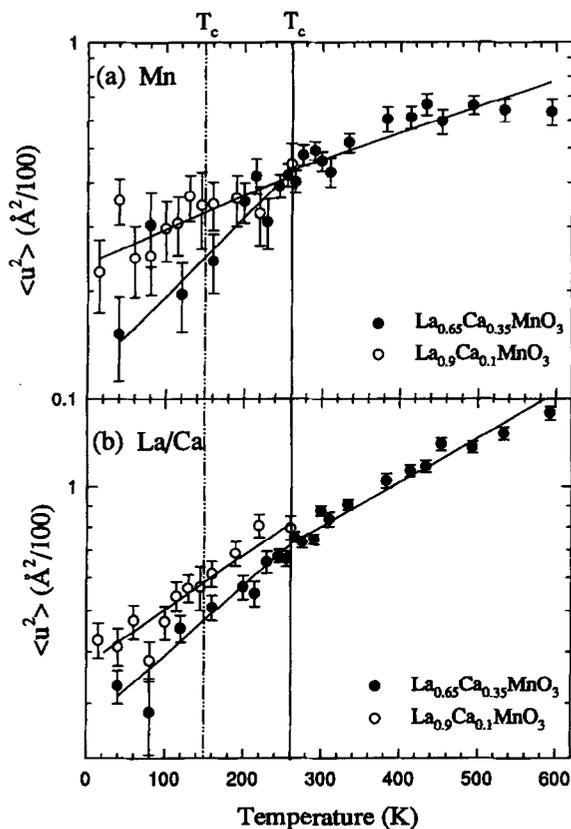


Fig. 4. Isotropic Debye-Waller factors vs  $T$  as obtained from Rietveld refinements for (a) Mn, (b) La/Ca. Solid lines are guides to the eye.

tested: (1) The effects of D-E and magnetic ordering (ferro- or antiferromagnetic) should be visible as a *kink* around  $T_c$  in resistance and Debye-Waller factors; and (2) the average oxygen *rms* displacements at low  $T$  should be larger than that of the medium electron-phonon coupling compounds, due directly to the trapping of the conduction band electrons by the J-T effect. It is true that the *rms* motion of the oxygen atoms is larger at low  $T$  in the strong coupling system (10% Ca-doping) than that of the medium coupling system (35% Ca-doping), but we observe no sign of a *kink* in the oxygen *rms* motion around  $T_c$  for the strong coupling system. One possible explanation for such behavior is that the static lattice effects due to the frozen-in J-T distortion with long range order may alter the electronic properties and hence diminish the effect of ferromagnetic ordering. Such a scenario is consistent with the small change observed near  $T_c$  from the bulk resistivity data [16, 17].

The results presented in this paper can be used to identify the role of the static/dynamic J-T distortion in the understanding of the microscopic origin of the CMR effect as well as magnetic phase transition in

these materials. From the data on the 10% compound, it is clear that the static/dynamic J-T effect is strong in this regime and the key to understanding the magnetic phase transition is the possible correlation between the ordering and the anomalous change in the interplanar thermal expansion at  $T_c$ . Such a behavior, however, was not found in the CMR compound where the in-plane thermal expansion and anomalous *rms* motion of the oxygen atoms are clearly important. This anomalous behavior in the CMR compound may be a direct consequence of the electron-phonon interaction proposed in the theories [5, 6]. If this is indeed the case, one would expect a large effect on the phonon dispersion and damping, particularly those associated with the motion of oxygen atoms. Work is currently in progress to address these issues.

In conclusion, we have studied the structural and magnetic phase transitions in perovskite  $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$  by neutron powder diffraction. Our results indicate that the compound has an orthorhombic structure at all temperatures investigated. Although this compound shows an anomalous response of the lattice parameters around  $T_c$ , the temperature dependence of the oxygen Debye-Waller factors show no anomaly at  $T_c$ , in clear contrast to its CMR counterpart  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ .

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