

Simultaneous Structural, Magnetic, and Electronic Transitions in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x = 0.25$ and 0.50

P. G. Radaelli,¹ D. E. Cox,² M. Marezio,^{3,4} S-W. Cheong,⁴ P. E. Schiffer,⁴ and A. P. Ramirez⁴

¹*Institut Max Von Laue-Paul Langevin, BP156, 38042 Grenoble Cedex 09, France*

²*Physics Department, Brookhaven National Laboratory, Upton, New York 11973*

³*Laboratoire de Cristallographie, CNRS/UJF, BP166, 38042 Grenoble Cedex 09, France*

⁴*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

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The magnetic transitions in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.25, 0.50$) were studied by synchrotron x-ray and neutron powder diffraction. For $x = 0.25$ the large $\Delta V = 0.13\%$ at T_C is due to the simultaneous insulator-to-metal transition. For $x = 0.50$ below T_C we observed a drastic decrease of the b axis and an increase of the a and c axes, due to a Jahn-Teller distortion of MnO_6 octahedra. The ferromagnetic transition for $x = 0.50$ is accompanied by an unusual peak broadening terminating at T_N . This newly observed behavior can be explained assuming that multiple intermediate phases are simultaneously present in the sample.

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There has been much recent interest in the close interplay between magnetism and transport properties in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [1-6]. As a function of temperature and doping, this system displays various magnetic transitions, some of which are associated with sharp changes of the electrical conductivity. In particular, much attention has been concentrated on the paramagnetic-to-ferromagnetic transition, for $x \sim 0.3$, associated with a sharp drop of resistivity. The Curie temperature can be increased in a magnetic field, thereby producing a giant magnetoresistance, traditionally ascribed to a double exchange mechanism. At higher doping levels ($x > 0.50$) the system is antiferromagnetic at low temperatures, and, in a narrow region of composition around $x = 0.50$, both types of magnetic order occur [7]. At high temperatures, the $x = 0.50$ compound is a paramagnetic insulator, and upon cooling it first becomes ferromagnetic (~ 225 K) and then antiferromagnetic (~ 155 K). This intriguing behavior has been attributed to the competition between ferromagnetic double exchange and antiferromagnetic superexchange coupling. In this paper we report on high-resolution synchrotron x-ray and neutron powder diffraction studies of selected compositions which reveal that both ferromagnetic and antiferromagnetic transitions are associated with significant lattice changes. For $x = 0.25$, the volume contraction at the transition suggests that this transition is first order. The magnetic transitions for $x = 0.50$ are highly unusual in that Bragg peaks show a unique evolution of peak shape with temperature. Our results clearly verify the striking interplay among spin, charge, and lattice degrees of freedom in the system.

The synthesis procedure for the samples with $x = 0.25$ and $x = 0.50$, along with a detailed study of the magnetic and electrical properties of these and other members of the series, will be published elsewhere [7]. X-ray powder diffraction data were collected on the X7A beamline

at the National Synchrotron Light Source at Brookhaven National Laboratory, using a wavelength of 0.7015 \AA . In order to determine the space group symmetry, extended regions of the powder pattern ($0^\circ < 2\theta \leq 40^\circ$) were collected for the two samples at 300 and 20 K. A Ge(220) analyzer crystal was employed in the diffracted beam, giving an instrumental resolution of $\sim 0.01^\circ$ over this 2θ range. Selected reflections were monitored as a function of decreasing temperature in order to obtain accurate lattice constants. In the case of the $x = 0.50$ sample, extended scans ($0^\circ < 2\theta \leq 83^\circ$) were collected at 300, 160, and 20 K on cooling, using a position-sensitive detector, having an instrumental resolution of $\sim 0.05^\circ$. Neutron diffraction data were collected from the $x = 0.5$ sample on the high-resolution powder diffractometer D2B at the Institut Laue-Langevin, using a wavelength of 1.594 \AA , in the high-intensity mode, with no primary beam collimation and $5'$ collimation between sample and detector. Full diffraction patterns ($5^\circ \leq 2\theta \leq 165^\circ$) were collected at 1.54, 55, 120, 170, 190, 230, and 300 K on warming. The complete x-ray and neutron patterns were analyzed using the GSAS program. Magnetization was measured using a commercial SQUID magnetometer, and resistivity was measured by a standard four-contact ac method.

Analysis of the full patterns and of individual reflections reveals that the $x = 0.25$ and 0.50 samples are metrically orthorhombic (i.e., $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$) at all temperatures. These lattice constants are related to the simple perovskite lattice parameter a_p by $a \approx c \approx \sqrt{2}a_p$ and $b \approx 2a_p$. For the x-ray data, the systematically absent reflections are consistent with the proposed space group $Pnma$ [8]. For the $x = 0.5$ sample a few very weak extra reflections were observed in the x-ray pattern below ~ 180 K. These peaks are quite broad compared to the fundamental peaks and cannot be indexed on the basis of the original unit cell.

The lattice parameters as a function of temperature are shown in Fig. 1 for $x = 0.25$ together with the magnetic susceptibility and electric resistivity. The figure clearly demonstrates the presence of a lattice contraction below 240 K, with an abrupt decrease of all lattice parameters and a volume discontinuity $\Delta V/V \approx 0.13\%$. As can be seen from the top panel, this temperature coincides well with T_C for this composition.

The large volume change at T_C is highly unusual and cannot be attributed simply to the development of FM spin order because lattice parameters for ferromagnetic 3d transition metals and their compounds at T_C change typically by 10–100 ppm. On the other hand, this is not simply a FM transition, as evidenced by the change from insulating to metallic behavior at T_C and the associated sharp drop in ρ . This change in the transport properties and the associated increase in the metallic nature of the bonds must therefore be responsible for the size of the volume change [9]. The abruptness of the transition in ρ and the seemingly discontinuous behavior in V suggest that the transition may be first order, although no evidence of hysteresis was seen in $M(T)$ or $\rho(T)$ to within the accuracy of our measurements (~ 1 K). A first-order

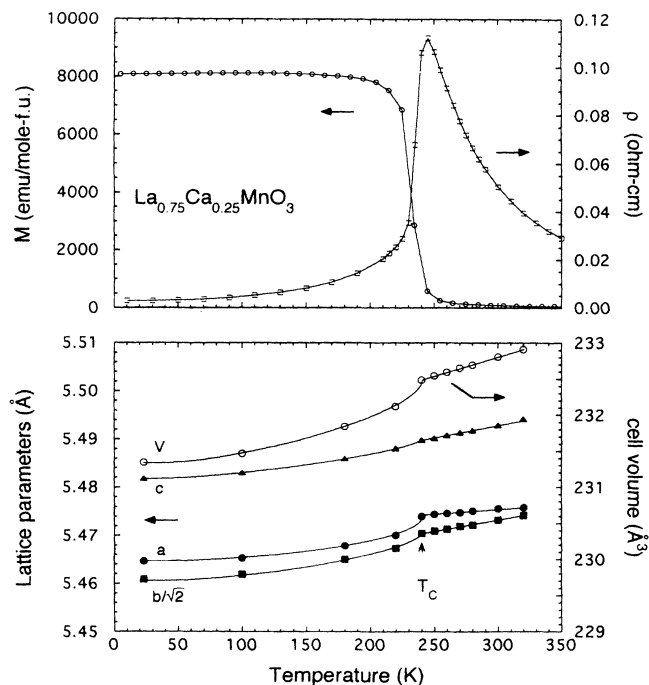


FIG. 1. Lower: Lattice parameters and cell volume of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ as a function of temperature as obtained from high-resolution synchrotron x-ray powder diffraction data. The error bars are smaller than the symbols. The scale for the lattice parameters is expanded with respect to Fig. 2. Lines through the points are guides to the eye. Upper: Magnetization ($H = 0.1$ T) and electric resistivity ($H = 0$ T) vs T for $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ (reprinted from Ref. [6]).

transition would be consistent with recent reports of such a transition in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [10].

The $x = 0.50$ sample shows much larger changes in the lattice parameters at the magnetic transitions. Throughout a relatively broad region with an onset at ~ 220 K the b lattice parameter drastically decreases, while those along the a and c axes increase. This behavior is accompanied by an increase of the a - c strain, i.e., $2(c - a)/(c + a)$. In Fig. 2 the lattice parameter variation vs temperature for $x = 0.50$ is shown together with that of the magnetization and resistivity. The onsets of the increase of a and c and of the decrease of the b parameter are associated with the inflection point in the $M(T)$ curve, defining the ferromagnetic transition. It is remarkable that no transition is observed in the V vs T curve. The subsequent intermediate regime of magnetization spans an interval of ~ 50 K, which is just in the range where a rapid decrease of the b axis and increase of the a and c axes occur. The sharp drop in the $M(T)$ curve occurring at ~ 170 K, accompanying a sharp increase of resistivity, is associated with the appearance of antiferromagnetic reflections in the neutron powder diffraction patterns, which can be indexed on a $2a \times b \times 2c$ supercell [11]. The integrated intensity of the (111) peak (the strongest magnetic reflection) as a function of temperature, shown in Fig. 3, demonstrates that antiferromagnetism is present

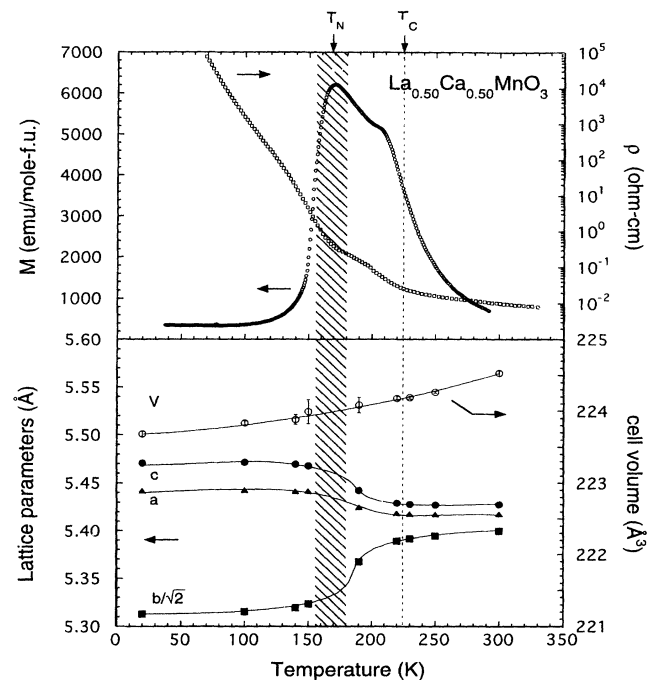


FIG. 2. Lower: Lattice parameters and cell volume as a function of temperature for the $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ sample, measured on cooling. Error bars are smaller than the symbols. Lines through the points are guides to the eye. The shaded area represents the width of the magnetization hysteresis loop. Upper: Magnetization ($H = 1$ T) and electric resistivity ($H = 0$ T) vs T for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ measured on cooling.

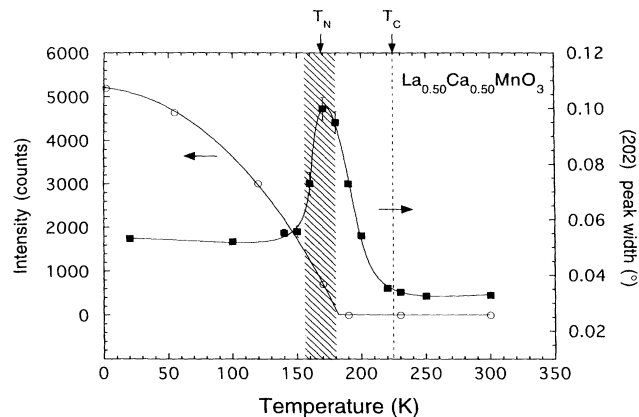


FIG. 3. Open circles represent the integrated intensity of the magnetic (111) peak as a function of temperature, measured on warming from neutron powder diffraction data. The magnetic cell has the lattice parameters a and c doubled with respect to the “nuclear” cell. Error bars are smaller than the symbols. Filled squares represent the peak width of the (202) nuclear synchrotron x-ray reflection as a function of temperature, measured on cooling. The lines are guides to the eye. The shaded area represents the width of the magnetization hysteresis loop.

up to 170 K, but is absent at 190 K and above. As implied by the Jahn-Teller distorted octahedra (see below) and a sharp rise of resistivity below the transition, a charge ordering should also take place at this transition. On the other hand, magnetization and resistivity measurements carried out on cooling and warming clearly evidenced a large hysteresis, indicating the strong first-order nature of the AFM transition [7]. Rietveld refinements based on both the x-ray and neutron powder diffraction data were carried out at various temperatures in order to determine the microscopic origin of the lattice change. Selected bond lengths and angles for $x = 0.50$ at 300 K and 1.54 K are reported in Table I. The main effect of the transition is a redistribution of the Mn-O bond lengths, rather than that of the bond angles. At room temperature, the octahedral coordination of manganese with oxygen is undistorted, with six almost equal Mn-O distances. At low temperature, the two Mn-O1 distances (along the b axis) become shorter than the four Mn-O2 distances in the a - c plane by ~ 0.04 Å. This effect would be consistent with a Jahn-Teller distortion of the Mn^{3+} ions of an “apically compressed” type (four long and two short Mn-O distances in the octahedron) with the short bond oriented along the b axis. However, if charge localization occurs this is only an average model, in which case a distortion of the “apically elongated” type (four short and two long), with two of the short bonds always oriented along the b axis, and the other two oriented along either the [101] or the $[\bar{1}01]$ axis with equal probability, would also be possible. Goodenough proposed the latter model, in conjunction with Mn^{3+} - Mn^{4+} orbital ordering, as an explanation for the observed magnetic structure

TABLE I. Selected bond distances and angles obtained from Rietveld refinements of neutron powder diffraction data for $x = 0.50$ at 1.54 and 300 K. Numbers in parentheses are statistical errors of the last significant digit.

Parameter	$T = 1.54$ K	$T = 300$ K
Mn-O1 (Å) ^a	1.9150(4)	1.9408(3)
Mn-O2 (Å) ^b	1.950(2)	1.939(2)
Mn-O2 (Å) ^b	1.964(2)	1.950(2)
Mn-O1-Mn (deg)	158.7(1)	160.15(9)
Mn-O2-Mn (deg)	161.56(9)	161.65(6)

^aAlong the b axis.

^bIn the a - c plane.

of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [12]. According to the Goodenough model, two of the short Mn^{3+} -O distances would be parallel to the b axis, while the other two would form zigzag $\dots\text{Mn}^{3+}\text{-O-Mn}^{4+}\text{-O}\dots$ chains in the a - c plane. The observed magnetic peaks would be consistent with an antiferromagnetic intrachain coupling, while the interchain coupling would be antiferromagnetic along the b axis and ferromagnetic in the a - c plane. However, the magnetic reflections associated with the Mn^{3+} sublattice display significant broadening, indicating that the antiferromagnetic chains have short coherence length (~ 300 Å). Furthermore, the extra peaks observed in the low-temperature x-ray patterns have peak widths ($\sim 0.2^\circ$), which correspond to the same coherence length, and show a similar dependence of intensity with temperature as the magnetic peaks. It therefore seems likely that these peaks result from a small distortion of the crystal structure associated with charge ordering, although the peak positions are not consistent with any simple enlargement of the unit cell.

The most dramatic aspect of the structural change occurring in the region between T_C and T_N is the unusual behavior of the peak widths through the transition. This phenomenon, being quite reproducible over a wide temperature region, cannot be attributed to temperature gradients across the sample nor to kinetics. Preliminary data indicate that the $x = 0.67$ sample also shows a similar but less significant effect. Figure 4 shows the evolution of the 202-040 Bragg reflections for $x = 0.50$ in the temperature region 250–150 K, where the largest change in lattice parameters takes place. The two Bragg reflections are seen to be quite sharp at 250 and 150 K, but broaden dramatically in between. In this intermediate region, they develop a pronounced structure, which is inconsistent with a typical particle size or strain effect. It is also not possible to explain the observed line shapes in terms of a two-phase coexistence model. In fact, between 200 and 180 K, intensity develops in a region of the pattern (around $2\theta = 21.6^\circ$) where none is present at either 250 or 150 K. The variation of the peak width of the (202) reflection as a function of temperature is shown in Fig. 3. The onset of the broadening is associated with T_C , and, between T_C and T_N , the broadening increases indicating that the reflection

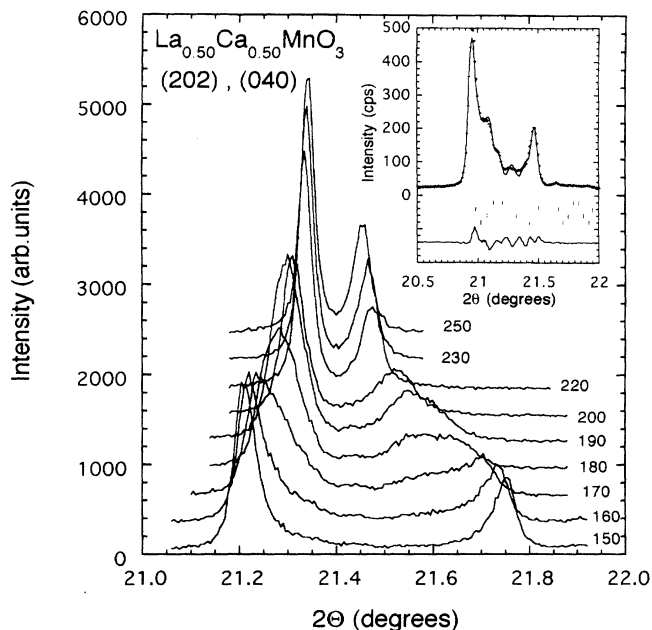


FIG. 4. Evolution of the 202-040 reflections as a function of temperature for the $x = 0.50$ samples, based on synchrotron x-ray powder diffraction data with a resolution $\Delta 2\theta \approx 0.01^\circ$. Inset: Portion of a full-pattern Rietveld fit to synchrotron x-ray powder diffraction data, obtained with a position-sensitive detector of resolution $\Delta 2\theta \approx 0.05^\circ$. The figure shows the 202-040 reflections fitted with four independent phases. Tick marks indicate the position of the Bragg peaks. The crosses (+) are observed data, while the solid line is the calculated profile. A difference curve (observed minus calculated) is plotted at the bottom.

splits and the splitting increases with decreasing temperature. At T_N the width abruptly decreases and then remains constant.

These observations can only be explained by either a continuous distribution of lattice parameters with several maxima, which evolves with temperature, or by a number of discrete phases each having a coherence length larger than the intrinsic coherence length for x rays (a few thousand Å), their relative proportions varying with temperature. A test of the latter model based on fitting the 202-040 doublet showed that at least four phases are necessary to obtain a satisfactory fit to the data at 160 K. This model was successfully used as a basis of subsequent Rietveld refinement analyses of the full pattern. A portion of the Rietveld plot, showing the 202-040 doublet fitted with four phases, is shown in the inset of Fig. 4. It is noteworthy that, although the four phases have differ-

ent lattice parameters, the corresponding unit cell volume is approximately equal for all of them. Although the exact cause of this very unusual effect is unclear, we speculate that the multiple "phases" may correspond to domains with different degrees of orientational order of the Jahn-Teller-distorted Mn^{3+}O_6 octahedra. In fact, as the local symmetry of the Mn^{3+} ions spontaneously decreases from approximately cubic to tetragonal, three equivalent ground states are possible, depending on the orientation of the half-filled $\text{Mn}-d_{z^2}$ orbital. In a real lattice, and for sufficiently large distortions, this degeneracy is lifted by the interplay between lattice energy and exchange interaction. However, in the transition region, several metastable configurations could be competing. These states would be intermediate between a complete orientational disorder of the $\text{Mn}-d_{z^2}$ orbitals, crystallographically indistinguishable from the undistorted high-temperature phase and a complete ordering in the a - c plane, corresponding to the low-temperature phase proposed by Goodenough [12]. In this hypothesis, the observed lattice strain effect would be the result of the simultaneous presence in different domains of several metastable states.

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