Crystal and magnetic structure of the La$_{1-x}$Ca$_x$MnO$_3$ compound ($x = 0.8, 0.85$).

M. Pissas, G. Kallias

Institute of Materials Science, NCSR, Demokritos, 153 10 Aghia Paraskevi, Athens, Greece

M. Hofmann, D. M. Többens

Berlin Neutron Scattering Center, Hahn-Meitner-Institut Glienicker Str. 100 D-14109, Berlin, Germany

(Dated: March 22, 2022)

We studied the crystal and magnetic structure of the La$_{1-x}$Ca$_x$MnO$_3$ compound for $x = 0.8$ and $x = 0.85$. At $T = 300$ K both samples are paramagnetic with crystallographic symmetry Pnma. At low temperatures they undergo a monoclinic distortion from orthorhombic Pnma-type structure with $a_p \sqrt{2} \times 2a_p \times a_p \sqrt{2}$ to a monoclinic structure with $(a_p \sqrt{2} \times 2a_p \times a_p \sqrt{2}, \beta = 90 + \varepsilon \sim 91.4^\circ)$ and $P2_1/m$ space group below $T_N$. The onset of the structural transformation coincides with the development of the C-type long range antiferromagnetic order with propagation vector $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$.

The monoclinic unit cell allowed us to determine the direction of the Mn magnetic moment with respect to the crystallographic axes: it is perpendicular to the propagation vector, $\mathbf{m} \perp \mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$.

The amplitude of the ordered magnetic moment at $T = 1.6$ K is found to be 2.53(2) and 2.47(2)$\mu_B$ for $x = 0.8$ and 0.85, respectively.

PACS numbers: 75.30 Vn, 25.40.Dn, 75.25.+z, 75.50.+E, 64.70.Kb

I. INTRODUCTION

The interest in the mixed perovskite family La$_{1-x}$Ca$_x$MnO$_3$ has been renewed in connection with the discovery of colossal magnetoresistance for $x \sim 0.33$. For the high doping range with $x > 0.5$, the Mn$^{3+}$ $e_g$ electrons become localized at low temperatures with a concomitant anisotropic bond reorganization in the oxygen environment of the manganites. This cooperative atomic rearrangement can change the symmetry or not, depending upon the particular electronic concentration, orbital occupancy, average size and distribution in the La site. Thus, when the temperature is lowered through a transition temperature $T_{co}$, charge and orbital ordering occur. Up to now two distinct cases of charge-ordering have been reported for $x = 0.50$ and $x = 0.67$ both by transmission electron microscopy and synchrotron x-ray and neutron powder diffraction.

At half-doping ($x = 0.50$), the system undergoes a phase transition from paramagnetic (insulating) to ferromagnetic-metallic (FM) phase at onset temperature $T_c = 234$ K and then upon cooling to an antiferromagnetic-insulating (AFM) phase at $T_N = 163$ K. The antiferromagnetic phase presents charge and spin ordered structure, called CE-type where real space ordering of Mn$^{3+}$ and Mn$^{4+}$ takes place. The basic characteristic of $x = 1/2$ phase, at low temperature, is the one after the other ordering of the Mn$^{3+}$ and Mn$^{4+}$ ions along the $a \approx \sqrt{2}a_p$ (Pnma setting, $a_p$ is the pseudo cubic unit cell parameter of the ideal cubic perovskite structure) leading to a superstructure with a propagation vector $\mathbf{k} = (2\pi/a)(1/2, 0, 0)$.

For $x = 0.67$ pioneer work of Radaelli and collaborators has shown a crystallographic charge-ordered and magnetic superstructure. The antiferromagnetic structure is noncollinear with the $a$ lattice parameter to be tripled and the $c$ lattice parameter to be doubled with respect to the average crystallographic unit cell Pnma setting. The crystallographic structure below the charge-ordering temperature ($T_{CO} \approx 260$ K) is characterized by ordering of the $d_{z^2}$ orbitals of the Jahn-Teller-distorted Mn$^{3+}$O$_6$ octahedron in the orthorhombic $ac$ plane, and the appearance of superlattice peaks in the x-ray patterns corresponding to a tripling of the $a$ axis lattice parameter. The refinement has revealed ordering of the Mn$^{3+}$ cations in sites as far apart as possible in the $ac$ plane “Wigner-crystal” model and transverse displacements of the Mn$^{3+}$O$_6$ octahedra in the $c$ direction. A recent study on $x = 2/3$ combining transmission electron microscopy with high resolution synchrotron powder x-ray diffraction data also supports the “Wigner crystal” model.

Moreover, transmission electron microscopy studies in La$_{1-x}$Ca$_x$MnO$_3$ with $x = 0.50, 0.625, 0.67, 0.75$ and 0.80 have shown superlattice reflections and their analysis pointed to a linear dependence between the magnitude of the modulation wave vector $\mathbf{q}_s$ along the $a$ axis and $x$, that is, $q_s = 1 - x$. However, the superlattice reflections of the charge-ordering for $x = 0.8$ were noticeably broader than lower compositions, indicating a very short coherence length.

Given the interplay of structural, transport, and magnetic properties on these highly correlated electron systems it is extremely important to provide information on the crystal and magnetic structure for $x$ values above 0.75, for which the existing literature is rather limited.

In the present paper we discuss the crystal and magnetic structure for doping levels near the end members of the La$_{1-x}$Ca$_x$MnO$_3$ homologous series using elastic neutron diffraction data from polycrystalline La$_{1-x}$Ca$_x$MnO$_3$ samples with $x = 0.8$ and 0.85. An important question that is been posed is whether charge...
mixed powders reacted in air in temperatures up to 1400°C. The neutron powder diffraction experiments as a function of temperature in the low angle regime were performed using the E6 and E9 diffractometers of the research reactor BER II in Berlin. The neutron powder diffraction data were collected on the E9 diffractometer with wavelength $\lambda = 1.798\text{Å}$, with collimation $\alpha_1 = 10/\text{°}$ (in pile collimator), $\alpha_2 = 20/\text{°}$ (second collimator after monochromator) and 64 x 10/° collimators in front of 64 °He single detector tubes. The powdered samples were placed in a cylindrical vanadium can ($D = 8 \text{ mm}$) mounted in an ILL orange cryostat. DC magnetization measurements were performed in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

III. CRYSTAL STRUCTURE

We performed Rietveld refinements of the nuclear and magnetic structures of neutron data using the FULLPROF program. The systematically absent reflections of the $x = 0.8, 0.85$ diffraction patterns at 300 K are consistent with space group $Pnma$. The crystal structure at 300 K was refined using as starting model the orthorhombic GdFeO$_3$ type structural model. First, the scale factor, background, unit cell parameters and zero-shift errors were optimized. The peak shapes are well described by function proposed by Finger, Cox and Jephcoat in order to model appropriately the high vertical apertures used in the beam geometry. Then, we refined the atomic positions and the isotropic thermal parameters. In the final step, we refined the oxygen thermal parameters anisotropically reducing further the refinement agreement parameters. Figure 1 shows as an example the observed and calculated neutron powder diffraction intensity patterns for the La$_{0.15}$Ca$_{0.85}$MnO$_3$ sample at 300 K. The corresponding structural parameters are reported in Table I and the selected bond distances in Table II.

The neutron diffraction patterns, below a temperature of 85 K shows a splitting of the $(111)$ reflection, characteristic for the existence of monoclinic distortion of the structure with the monoclinic angle $\beta > 90^\circ$. In the case of a monoclinic distortion of the unit cell, one expects a splitting of the reflections (111) and $(11\bar{1})$, $d^{-2}(111)-d^{-2}(11\bar{1}) \propto -\cos \beta$, since the cross term $hl$ in the expression for the d-spacing for these reflections is non zero.

The structure at $T = 300$ K is associated with the GdFeO$_3$/CaTiO$_3$ type structures (like the samples with different Ca content) and is derived from the cubic perovskite by a combination of MnO$_6$ octahedra tilts (Glazer notation $Pnma$, $a^-b^a^-c^+a^-$). Looking in

FIG. 1: Rietveld refinement for La$_{0.15}$Ca$_{0.85}$MnO$_3$ at 300 K ($\lambda = 1.798\text{Å}$). The observed data points are indicated with open circles, while the calculated pattern is shown as a continuous line. The positions of the reflections are indicated with vertical lines below the pattern.

II. EXPERIMENTAL DETAILS

La$_{1-x}$Ca$_x$MnO$_3$ samples with $x = 0.80$ and $x = 0.85$ were prepared by thoroughly mixing high purity stoichiometric amounts of CaCO$_3$, La$_2$O$_3$, and MnO$_2$. The mixed powders reacted in air in temperatures up to 1400°C for several days with intermediate grindings. Finally the sample was slowly cooled to room temperature. Neutron diffraction data were collected on the E6 and E9 diffractometers of the research reactor BER II in Berlin. The neutron powder diffraction experiments as a function of temperature in the low angle range were performed in diffractometer E6 using a wavelength $\lambda = 2.44\text{Å}$ ((002) reflection of a pyrolytic graphite monochromator). For crystal structure refinement, data were collected on the E9 diffractometer with wave length $\lambda = 1.798\text{Å}$ ((511) reflection of a vertically focusing Ge monochromator), with collimation $\alpha_1 = 10/\text{°}$ (in pile collimator), $\alpha_2 = 20/\text{°}$ (second collimator after monochromator) and 64 x 10/° collimators in front of 64 °He single detector tubes. The powdered samples were placed in
Glazer’s classification for an octahedral tilt system which maintains the tilt system $a^{-b^+c^-}$ and is compatible with a monoclinic unit cell, we selected the tilt system $a^{-b^+c^-}$ to refine the low temperature monoclinic phase. This tilt system is described with the monoclinic space group $P2_1/m$, which is a subgroup of $P nma$. In $P2_1/m$ space group there are two non-equivalent sites for La and Mn. Each Mn site has its own apical oxygen (bond direction mainly along $b$-axis). Concerning the two plane oxygens at the general position they are shared by the two Mn sites. In order to reduce the free parameters we used the constrains $B$(La(1)) = $B$(La(2)) and $B$(Mn(1)) = $B$(Mn(2)) for La and Mn temperature factors respectively. The refinement of neutron diffraction patterns after taken the above constraints into consideration gives very good Rietveld agreement factors. The same type of monoclinic distortion has been observed in $Sm_{0.15}Ca_{0.85}MnO_3$ and $Bi_{0.15}Ca_{0.85}MnO_3$ compounds. Due to the low x-ray scattering factor of oxygen the experiments done by Zheng et al. were not sensitive enough to find the correct structural transition in $La_{0.15}Ca_{0.85}MnO_3$.

We have also tested the space group $P2_1/n$ (No 14) which follows the tilt system $a^{-b^-c^-}$ with an 1 : 1 ordering of the Mn ions. However, this model is not able to account for the peak at $2\theta \approx 43.5^\circ$, as well as for several other peaks at the high angles. We were therefore led to rule out this possibility. Recently Lobanov et al. reported that the ferromagnetic insulating $La_{0.85}Ca_{0.15}MnO_3$ compound undergoes a monoclinic distortion below the ferromagnetic transition (space group $P2_1/c$) with nonequivalent $MnO_2$ layers alternating along the $a$ axis. In their model they considered that the monoclinic angle is between the $b$ and $c$ axis of the high temperature $Pnma$ structure. From the specific pattern of Mn-O distances they proposed an unconventional orbital ordering. We tested also this model but since it does not predict splitting of the (202) reflection it can not account for the low temperature diffraction pattern of $La_{0.15}Ca_{0.85}MnO_3$. Figure 3 shows the observed and calculated neutron powder diffraction intensity patterns for $La_{0.15}Ca_{0.85}MnO_3$ at 1.6 K (the plot for $x = 0.8$ was similar) using neutron diffraction data from E9 diffractometer. The corresponding structural parameters for both samples are reported in Table I and the selected bond distances in Table II. The bonds’ length

FIG. 2: Observed and calculated neutron powder diffraction intensity patterns at $T = 1.6$ K and neutron diffraction patterns at 50 K, 100 K, 150 K and 165 K of the $La_{0.15}Ca_{0.85}MnO_3$ sample ($\lambda = 2.44\AA$). The observed data points are indicated with solid circles, while the total structural and magnetic calculated pattern are shown as continuous lines. The positions of the reflections for the crystal and magnetic structure employed in the refinements are indicated with vertical lines below the pattern. The indices refer to the magnetic reflections. The splitting of the (111) reflection (at 43 degrees) due to the monoclinic distortion can also be seen.
TABLE I: La$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.8$ and 0.85) structural parameters at $T = 300$ and 1.6 K as determined from Rietveld refinements based on neutron powder diffraction data of the E9 diffractometer ($\lambda = 1.798$ Å). The space group $Pmna$ (No 62) was used for the data at $T = 300$ K. La, Ca and apical oxygen (Oa) occupy the 4c, (x, 1/4, z) site, Mn the 4b (0, 0, 1/2) site and the plane oxygen (Op) the general 5d site. The monoclinic space group $P2_1/m$ (b axis unique No 11) was used for the data at $T = 1.6$ K. The atomic sites for $P2_1/m$ are: La/Ca1.2, Oa1.2 2e[x, z, z], Mn1 2b[0, 0, 0], Mn2 2e[0, 0, $\frac{1}{2}$], and Op1.2 4f[x, y, z]. The parameters $U_{ij}$ represent the eigenvalues of the cartesian $U$– matrix. Numbers in parentheses are statistical errors referring to the last significant digit.

| $x$ | 0.8 | 0.85 |
|-----|-----|------|
| $T$ (K) | 300 | 1.6 | 300 | 1.6 |
| $a$ (Å) | 5.3386(1) | 5.3529(2) | 5.3243(1) | 5.3556(1) |
| $b$ (Å) | 7.5376(1) | 7.4648(3) | 7.5193(1) | 7.4506(1) |
| $c$ (Å) | 5.3367(1) | 5.3506(2) | 5.3180(1) | 5.3258(1) |
| $\beta^\circ$ | 90 | 91.502(2) | 90 | 91.141(1) |
| La1 $x$ | 0.0240(7) | 0.02(2) | 0.0247(7) | 0.029(1) |
| $z$ | -0.006(1) | -0.005(1) | -0.009(1) | -0.005(1) |
| $B$ (Å$^2$) | 1.13(6) | 0.79(7) | 0.89(6) | 0.70(5) |
| La2 $x$ | 0.522(2) | 0.528(1) |
| $z$ | 0.509(2) | 0.509(1) |
| $B$ | 0.81(7) | 0.70(5) |
| Mn1 $B$ | 0.80(7) | 0.43(7) | 0.49(6) | 0.37(6) |
| Mn2 $B$ | - | 0.43(7) | - | 0.37(6) |
| O1a $x$ | 0.4921(8) | 0.497(2) | 0.4913(7) | 0.495(1) |
| $z$ | 0.063(1) | 0.061(1) | 0.061(1) |
| $U_{11}$ (Å$^2$) | 0.014(4) | 0.006(3) | 0.013(6) | 0.015(1) |
| $U_{22}$ | 0.0041(3) | 0.001(1) | 0.008(7) | 0.002(1) |
| $U_{33}$ | 0.0095(4) | 0.011(1) | 0.010(4) | 0.010(2) |
| O2a $x$ | 0.988(2) | 0.985(1) |
| $z$ | 0.438(1) | 0.434(1) |
| $U_{11}$ | 0.006(3) | 0.015(3) |
| $U_{22}$ | 0.001(1) | 0.002(1) |
| $U_{33}$ | 0.011(1) | 0.010(3) |
| O1p $x$ | 0.2827(7) | 0.282(1) | 0.2828(6) | 0.2829(8) |
| $y$ | 0.0414(4) | 0.038(3) | 0.0338(5) | 0.0342(8) |
| $z$ | 0.7155(8) | 0.721(1) | 0.7151(7) | 0.7198(9) |
| $U_{11}$ | 0.0075(3) | 0.022(2) | 0.0001 | 0.011(2) |
| $U_{22}$ | 0.0114(8) | 0.006(1) | 0.01638 | 0.003(1) |
| $U_{33}$ | 0.0202(5) | 0.003(1) | 0.0174 | 0.007(5) |
| O2p $x$ | 0.781(1) | 0.7842(8) |
| $y$ | 0.028(1) | 0.0308(6) |
| $z$ | 0.779(1) | 0.782(1) |
| $U_{11}$ | 0.022(2) | 0.011(2) |
| $U_{22}$ | 0.006(1) | 0.003(1) |
| $U_{33}$ | 0.003(1) | 0.007(1) |
| $R_p$ | 6.86 | 7.7 | 6.9 | 6.6 |
| $R_{wp}$ | 9.25 | 9.9 | 9.7 | 9.2 |
| $R_B$ | 6.35 | 4.86 | 5.09 | 4.82 |
| $\mu_e$ | 1.79(1) | 1.79(1) | 1.73(1) |
| $\mu_p$ | -1.79(1) | -1.73(1) |
| $\mu$ | 2.53(2) | 2.47(2) |
| $R_B(m)$ | 6.8 | 6.59 |
The main effect of the transition at $T_c$ 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 approximately undistorted, with four short bonds $\sim 1.91\,\text{Å}$ (two in the basal plane and two along $b$–axis) and two longer bonds $\sim 1.92\,\text{Å}$ in the basal plane. Upon cooling below $T_c$, the structural changes are evident in the MnO$_6$ octahedra. The two crystallographically independent MnO$_6$ octahedra are tetragonally elongated with the two Mn-O$_2p$ bonds in the $a-c$ plane elongated and four short bonds (Mn-O$p$ and Mn-O$o$) along the $b$–axis and $a-c$ plane respectively. This is also the manifestation of the static Jahn-Teller effect. The two manganese sites present in the monoclinic phase have very similar environments, except for the distortion parameter (see Table I), which is different by one order of magnitude. This fact may imply that the monoclinic phase displays orbital ordering but it does not show the typical signature of charge ordering. This orbital ordering is developed concomitantly with the antiferromagnetic ordering (see next section). Due to absence of large local distortions in the MnO$_6$ octahedra one can say that the high temperature phase undergoes a homogeneous distortion at $T= T_c$ and in the low temperature monoclinic structure the $e_g$ electrons are not definitely localized (absence of charge ordering). At this point we must note that the charge ordering model can not rule out completely because, the difference in the structural parameters for the charge ordering model at the studied concentrations ($x = 0.8, 0.85$) may by small.

The presence of two long bonds for both Mn sites at the monoclinic phase is a result of the fact that the $e_g$ electrons are $\sigma$-antibonding and any localization or confinement of them to a specific plane or direction will result in an expansion of the bonds in that directions. Delocalization of the $e_g$ electrons should lead to a very isotropic distribution of Mn-O distances in agreement with our observation above $T_c$.

Figure 4 shows the variation of the lattice parameters $a, b/\sqrt{2}$ and $c$ with temperature for both samples. The lattice parameters display changes below $T_{\text{max}}$. The $b$–axis undergoes a drastic decreasing while the $a$ and $c$ axes slightly increase. Since $a > c > b/\sqrt{2}$ the $x = 0.8$ and 0.85 samples belong to the so-called $O^\prime$ structure. This type of structure can result from octahedral tilting and a cooperative JT distortion (orbital ordering). For comparison we include in this figure the temperature variation of the magnetic moment deduced from the SQUID measurements during cooling, for both samples (see right scale). Both measurements display a maximum at $T_{\text{max}} = 210\,\text{K}$ and $160\,\text{K}$ for $x = 0.8$ and 0.85 samples, respectively. The observed magnetization peak can be explained by considering that at high temperatures the hopping of the $e_g$ electron induces ferromagnetic correlations through the double-exchange mechanism and when these electrons freeze the ferromagnetic fluctuations are replaced by superexchange driven antiferromagnetic spin fluctuations. Figure 4 shows the variation of the monoclinic angle $\beta$ as a function of temperature for both samples. In the same plot we include the temperature variation of the ordered magnetic moment per Mn ion (deduced from the magnetic peak intensity in neutron diffraction, see next section) for both samples. The monoclinic angle increases from $90^\circ$ at $T_c$ to $\sim 91^\circ$ at low temperatures and follows the temperature variation of the ordered magnetic moment shown in fig. 5. Also, the transition point marked by the appearance of the monoclinic distortion coincides with the peak observed in the SQUID data (fig. 4). The space group describing the low temperature structure is a maximal subgroup of the high temperature phase. Then, according the Landau theory of phase transitions one expect that the transition is of second order. In other words it is possible to go from the $Pnma$ structure to $P2_1/m$ by a continuous change in the cation displacements.

Finally, we discuss the possibility that the Mn(2) sites are occupied exclusively by Mn$^{+4}$ ions. The Mn(1) sites with longest bond length $\sim 1.95\,\text{Å}$ ($x = 0.80$ sample) corresponds to a site with a Mn$^{+3}$ character. For example it can be considered as randomly occupied by 60% Mn$^{+4}$ and 40% Mn$^{+3}$. Of course the Mn$^{+4}$–O bond length is
shorter by $\sim 0.05\text{Å}$ in comparison with $x = 0.5$ or $2/3$. The distortion is smaller for the sample with $x = 0.85$ than for that with $x = 0.80$. Therefore, we might conclude that if at $x = 0.75$ a clear charge-ordered state exists then when Ca content is further increased, the crystal is tending more and more to acquire the structure of CaMnO$_3$ with a homogeneous distortion of the $T = 300$ K $Pnma$ phase.

A. Magnetic structure

In this section we will discuss the magnetic reflections appearing at $T < T_c$ using neutron diffraction data from the E6 diffractometer. Figure 2 shows the neutron diffraction patterns of the La$_{0.15}$Ca$_{0.85}$MnO$_3$ sample recorded with $\lambda = 2.44\text{Å}$ in the range $1.6 - 165$ K. Below $T_c = 150$ K splitting of the family of peaks [(010), (020)] and (111) due to the monoclinic distortion is observed. A series of additional Bragg peaks occurring mainly at low angles give a clear indication for the presence of antiferromagnetic long-range ordering. The antiferromagnetic ordering occurs concomitantly with the monoclinic transition at $T_c$ ($T_N = T_c$). All the magnetic peaks can be indexed using the propagation vector $\mathbf{k} = \left(\frac{1}{2}, 0, \frac{1}{2}\right)$ (U point of the first Brillouin zone). The magnetic structure for this propagation vector corresponds to the so-called type-C antiferromagnetic structure.

The integrated intensity of a magnetic reflection at $\mathbf{q} = \mathbf{Q} + \mathbf{k}$ ($\mathbf{Q}$ is a reciprocal lattice vector) for a collinear magnetic structure in a neutron powder diffraction pattern can be written as:

$$I(\mathbf{q}) = \frac{I_0}{V^2} \frac{1}{\sin \theta \sin 2\theta} m \langle 1 - (\mathbf{q} \cdot \mathbf{s})^2 \rangle |F(\mathbf{q})|^2$$

(1)

where $I_0$ is the scale factor, $V$ is the unit cell volume, $\theta$ is the Bragg angle and $m$ is the multiplicity of the reflection $\mathbf{q}$. The term $\langle 1 - (\mathbf{q} \cdot \mathbf{s})^2 \rangle$ is an average over all the equivalent $\mathbf{q}$ reflections, $\mathbf{q}$ is the unit scattering vector, $\mathbf{s}$ is the unit vector along the axis of the collinear magnetic structure and $F(\mathbf{q})$ is the magnetic structure factor for the configurational symmetry. The magnetic structure factor for the particular crystal and magnetic structure can be written as

$$F(\mathbf{q}) = \{1 - \exp(\pi i k)\} \left\{ p_1 \exp \left[ \pi i \left( h + \frac{1}{2} \right) \right] + p_2 \exp \left[ \pi i \left( l + \frac{1}{2} \right) \right] \right\}$$

(2)

where $p_j = (0.269 \times 10^{-12}\text{cm/μB}) \times S_j \times f_j \times \exp(-W_j)$. $S_1$ ($S_2$) is the average ordered magnetic moment in Bohr magnetons $\mu_B$ for the Mn ion at (1/2,0,0) site ((0,0,1/2), $f_j$ is the magnetic form factor for the Mn ion and $W_j$ is the Debye-Waller factor for the $j$th Mn ion. Thanks to the monoclinic distortion the diffraction pattern revealed zero intensity for the resolved reflections $\left(\frac{1}{2}, \pm 1, -\frac{1}{2}\right)$ and $\left(\frac{1}{2}, \pm 1, \frac{1}{2}\right)$, $\left(\frac{1}{2}, \pm 1, \frac{1}{2}\right)$. Using Eq. 2 we can readily conclude that $p_1 = p_2$. The ferromagnetic interactions occur along the two long in-plane Mn-O bonds, while along the four short Mn-O bonds the interactions are antiferromagnetic. The relative intensity of the reflections $\left(\frac{1}{2}, \pm 1, \frac{1}{2}\right)$ and $\left(\frac{1}{2}, \pm 1, \frac{1}{2}\right)$ implies that $\mathbf{S} \perp \mathbf{k}$, that is, the magnetic moment is directed along the two long in-plane Mn-O bonds. The fit of the experimental pattern at $T = 1.6$ K gives an amplitude for the ordered magnetic moment per Mn ion of 2.53(2) and 2.47(1) $\mu_B$ for $x = 0.8$ and 0.85, respectively. These values are smaller than those that have been theoretically expected for the stoichiometric mixtures of Mn$^{4+}$ and Mn$^{3+}$ (e.g. $0.15 \times 4 + 0.85 \times 3 = 3.15$). The smaller observed magnetic moment than their nominal value of random mixture indicate the hybridization of the Mn $t_{2g}$ orbitals and the O 2p orbitals. The temperature variation of the ordered magnetic moment per Mn ion as obtained from Rietveld refinement of the neutron powder diffraction data

IV. CONCLUSIONS

The present work based on the analysis of neutron powder diffraction data shows that $x = 0.80$ and $x = 0.85$ undergo an orthorhombic-to-monoclinic structural transition around 210 K and 160 K, respectively. The monoclinic distortion is larger for the $x = 0.80$ sample. Simultaneously, long range antiferromagnetic order is developed and it can be described with propagation vector $\mathbf{k} = \left(\frac{1}{2}, 0, \frac{1}{2}\right)$ that corresponds to the C-type structure. The ordered magnetic moment of the Mn ions is found to be normal to the propagation vector.

A key question was about the existence or not of charge-ordering at low temperatures. Charge-ordering models without or with monoclinic distortions have failed to refine the diffraction patterns. The refinement was successful only with the $P2_1/m$ space group, where the two Mn sites in the low temperature structure have similar environments (in terms of their bond lengths in the corresponding MnO$_6$ octahedra). This absence of preferential local distortions (which would be a sign of different charges in the two Mn sites) in the MnO$_6$ octahedra have led us to conclude that charge-ordering does not
FIG. 5: Monoclinic angle $\beta$ and ordered magnetic moment per Mn ion as a function of temperature for La$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.8, 0.85$) as obtained from the neutron diffraction data. The continuous lines are guides for the eye. Error bars are smaller than the symbols.

This work was partially supported from the Greek Secretariat for Research and Technology through the PENED program 99ED186 and by the EC through the CHRX-CT93-0116 access to large-scale facilities project.

1. E. O. Wollan and W. C. Koehler, Phys. Rev. 100, 545 (1955).
2. J. B. Goudinough, Phys. Rev. 100, 564 (1955).
3. P. Schiffer, A. P. Ramirez, W. Bao, and S. -W. Cheong, Phys. Rev. Lett. 75, 3336 (1995).
4. H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, Science 270, 961 (1995).
5. Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. 11, 5108 (1995).
6. J. W. Lynn, R.W. Erwin, J. A. Borchers, Q. Huang, A. Santoro, J-L. Peng, and Z. Y. Li, Phys. Rev. Lett. 76, 4046 (1996).
7. A. P. Ramirez, P. Schiffer, S. -W. Cheong, C. H. Chen, W. Bao, T. T. Palstra, P. L. Gammel, D. J. Bishop, and B. Zegarski, Phys. Rev. Lett. 76, 3188 (1996).
8. S. Satpathy, Z. S. Popovic, and F. R. Vukajlovic, Phys. Rev. Lett. 76, 960 (1996).
9. A. J. Millis, Nature 392, 147 (1998).
10. E. L. Nagaev, Uspeh. Fiz. Nauk 166, 833 (1996); E. L. Nagaev, Physics-Uspehki 39, 781 (1996).
11. P. Majumdar and P. Littlewood Phys. Rev. Lett. 81, 1314 (1998).
12. A. Moreo, S. Yunoki, and E. Dagotto, Science 283, 2034 (1999).
13. G. Varelogiannis, Phys. Rev. Lett. 85, 4172 (2000).
14. A. P. Ramirez, J. Phys.: Condens. Matter 9, 8171 (1997).
15. C. N. R. Rao, Anthony Arulraj, A. K. Cheetham and Bernard Raveau, J Phys.:Condens. Matter 12, 83 (2000).
16. M. Pissas, G. Kallias, E. Devlin, A. Simopoulos, and D. Niarchos, J. Appl. Phys. 81, 8 (1997).
17. R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. 71, 2331 (1993).
18. P. G. Radaelli, D. E. Cox, M. Marezio, and S-W. Cheong, Phys. Rev. B 55, 3015 (1997); P. G. Radaelli, G. Iannone, M. Marezio, H. Y. Hwang, S-W. Cheong, J. D. Jorgensen, and A. N. Argyriou, Phys. Rev. B 56, 8265 (1997).
19. C. H. Chen and S-W. Cheong, Phys. Rev. Lett. 76, 4042 (1996); C. H. Chen, S-W. Cheong, and H. Y. Hwang, J. Appl. Phys. 81, 4326 (1997).
20. S. Mori, C. H. Chen, and S.-W.Cheong, Nature 492, 473 (1998).
21. S. Mori, C. H. Chen, and S.-W.Cheong, Nature 492, 473 (1998).
22. G. Varelogiannis, Phys. Rev. Lett. 85, 4172 (2000).
23. A. P. Ramirez, J. Phys.: Condens. Matter 9, 8171 (1997).
24. C. N. R. Rao, Anthony Arulraj, A. K. Cheetham and Bernard Raveau, J Phys.:Condens. Matter 12, 83 (2000).
25. M. Pissas, G. Kallias, E. Devlin, A. Simopoulos, and D. Niarchos, J. Appl. Phys. 81, 8 (1997).
26. R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. 71, 2331 (1993).
27. P. G. Radaelli, D. E. Cox, M. Marezio, and S-W. Cheong, Phys. Rev. B 55, 3015 (1997); P. G. Radaelli, G. Iannone, M. Marezio, H. Y. Hwang, S-W. Cheong, J. D. Jorgensen, and A. N. Argyriou, Phys. Rev. B 56, 8265 (1997).
28. C. H. Chen and S-W. Cheong, Phys. Rev. Lett. 76, 4042 (1996); C. H. Chen, S-W. Cheong, and H. Y. Hwang, J. Appl. Phys. 81, 4326 (1997).
29. S. Mori, C. H. Chen, and S.-W.Cheong, Nature 492, 473 (1998).
30. S. Mori, C. H. Chen, and S.-W.Cheong, Nature 492, 473 (1998).
31. G. Varelogiannis, Phys. Rev. Lett. 85, 4172 (2000).
Rev. B 58, 5185 (1998); W. Cheong, P. E. Schiffer, and A. P. Ramirez, Phys. Rev. Lett. 75, 4488 (1995).

G. Kallias, M. Pissas and A. Hoser, Physica B 276-278, 778 (2000).

Q. Huang, J. W. Lynn, R. W. Erwin, A. Santoro, D. C. Dender, V. N. Smolyaninova, K. Ghosh, and R. L. Greene, Phys. Rev. B, 61, 8895 (2000).

Renhu Wang, Jianian Gui, Yimei Zhu, and A. R. Moodenbaugh, Phys. Rev. B 61, 11946 (2000).

J. Q. Li, M. Uehara, C. Tsuruta, Y. Matsui, and Z. X. Zhao.

J. Rodriguez-Carvajal, Physica B 192, 55 (1993).

L. W. Finger, D. E. Cox, A. P. Jephcoat, J. Appl. Cryst. 27, 892 (1994).

D. M. Többens, N. Stüsser, K. Knorr, H. M. Mayer, G. Lampert, Mater. Sci. Forum in press.

A. Glazer, Acta Cryst. B28, 3384 (1972).

P. M. Woodward, Acta Cryst. B53, 32 (1997).

C. Martin, A. Maignan, M. Hervieu, B. Raveau, Z. Jiráček, A. Kurbakov, V. Troumov, G. André, F. Bourée, J. Magn. and Magn. Matter., 205, 184 (1999).

A. Llobet, C. Frontera, J. L. Carci-Muñoz, C. Ritter, M. A. G. Aranda, Chem. Mater. 12, 3648 (2000).

R. K. Zheng, C. F. Zhu, J. Q. Xie and X. G. Li, Phys. Rev. B 63, 024427.

M. V. Lobanov, A. M. Balagurov, V. Ju. Pomjakushin, P. Fischer, M. Gutmann, A. M. Abakumov, O. G. D’yachenko, E. V. Antipov, O. I. Lebedev, and G. Van Tendeloo, Phys. Rev. B, 61, 8941 (2000).

F. Moussa, M. Hennion, J. Rodriguez-Carvajal, H. Moudden, L. Pinsard, and A. Revcolevschi, Phys. Rev. B 54, 15149 (1996); Q. Huang, A. Santoro, J. W. Lynn, R. W. Erwin, J. A. Borchers, J. L. Peng, and R. L. Greene, Phys. Rev. 55, 14987 (1997).

P. Dai, J Zhang, H. A. Mook, S.-H. Liou, P. A. Dowben, and E. W. Plummer, Phys. Rev. B 54, R3694, (1996).

Statistical Physics Part I, Course of Theoretical Physics by L. D. Landau and E. M. Lifshitz, 2nd edition, Pergamon Press.
TABLE II: Selected bond lengths (Å) and bond angles (deg) for La$_{1-x}$Ca$_x$MnO$_3$ (x = 0.8, 0.85) samples at T = 1.6 and 300 K, calculated according to the structural parameters presented in Table I. At 300 K (1.6 K) the structural model predicts one (two) Mn sites. The bond with subscript 'a' denotes bond mainly along the b-axis, while the 'p' stands for bonds in the a−c plane. The table also includes the average bond length $< d > = (1/6) \sum_{i=1,6} d_i$, the distortion parameter of the MnO$_6$ octahedra $s_2^2 = (1/6) \sum_{i=1,6} (d_i - < d >)/ < d > ]^2$.

| $T$ (K) | 0.8  | 1.6  | 0.8  | 1.6  |
|---------|------|------|------|------|
| Mn-Oa × 2 | 1.915(1) | - | 1.908(1) | - |
| Mn-Op × 2 | 1.925(1) | - | 1.923(3) | - |
| Mn-Op × 2 | 1.912(4) | - | 1.908(3) | - |
| Mn(1)-O1a × 2 | - | 1.895(1) | - | 1.894(1) |
| Mn(1)-O1p × 2 | - | 1.886(5) | - | 1.867(1) |
| Mn(1)-O2p × 2 | - | 1.952(7) | - | 1.941(5) |
| Mn(2)-O2a × 2 | - | 1.895(1) | - | 1.898(1) |
| Mn(2)-O1p × 2 | - | 1.920(6) | - | 1.909(4) |
| Mn(2)-O2p × 2 | - | 1.931(6) | - | 1.925(5) |
| Mn(1)-O1a-Mn(1) | 159.3(3) | 159.9(5) | 160.0(4) | 159.8(4) |
| Mn(2)-O2a-Mn(2) | - | 159.7(5) | - | 158.3(4) |
| Mn(2)-O1p-Mn(1) | 159.1(2) | 157.5(4) | 158.3(2) | 158.7(3) |
| Mn(2)-O1p-Mn(1) | - | 161.5(3) | - | 159.8(5) |
| La-Oa × 2 | 2.369(6) | - | 2.344(6) | - |
| La-Oa × 1 | 2.37(1) | - | 2.38 (1) | - |
| La-Op × 2 | 2.527(6) | - | 2.513(6) | - |
| La-Op × 2 | 2.610(6) | - | 2.583(6) | - |
| La-Op × 2 | 2.640(5) | - | 2.651(6) | - |
| La-Oa × 1 | 2.864(6) | - | 2.864(6) | - |
| La-Oa × 1 | 2.97(1) | - | 2.94 (1) | - |
| La-Op × 2 | 3.098(6) | - | 3.112(6) | - |
| La(1)-O2p × 2 | - | 2.374(9) | - | 2.36 (1) |
| La(1)-O2a × 1 | - | 2.38(1) | - | 2.35 (1) |
| La(1)-O1a × 1 | - | 2.55 (1) | - | 2.50 (1) |
| La(1)-O1p × 2 | - | 2.58 (1) | - | 2.583(6) |
| La(1)-O2p × 2 | - | 2.613(8) | - | 2.595(6) |
| La(1)-O1a × 1 | - | 2.84 (1) | - | 2.87 (1) |
| La(1)-O2a × 1 | - | 2.97(1) | - | 2.98 (1) |
| La(1)-O1p × 2 | - | 3.122(9) | - | 3.114(7) |
| La(2)-O1p × 2 | - | 2.34 (1) | - | 2.370(9) |
| La(2)-O1a × 1 | - | 2.39(1) | - | 2.38 (1) |
| La(2)-O2a × 1 | - | 2.53 (1) | - | 2.48 (6) |
| La(2)-O2p × 2 | - | 2.57 (1) | - | 2.564(7) |
| La(2)-O1p × 2 | - | 2.705(6) | - | 2.654(7) |
| La(2)-O2a × 1 | - | 2.87 (1) | - | 2.91 (1) |
| La(2)-O1a × 1 | - | 2.96(1) | - | 2.95 (1) |
| La(2)-O2p × 2 | - | 3.038(9) | - | 3.077(7) |

$< d_1 >$ | 1.917(2) | 1.911(2) | 1.913(2) | 1.907(2) |
$< d_2 >$ | 1.915(2) | 1.910(2) |
$< s_2^2 > \times 10^{-5}$ | 1.61 | 44.68 | 2.6 | 30.14 |
$< s_1^2 > \times 10^{-5}$ | 7.95 | 6.45 |