Phase diagram of the La$_{1-x}$Ca$_x$MnO$_3$ compound for $0.5 \leq x \leq 0.9$.

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We have studied the phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ for $0.5 \leq x \leq 0.9$ using neutron powder diffraction and magnetization measurements. At 300 K all samples are paramagnetic and single phase with crystallographic symmetry $Pnma$. As the temperature is reduced a structural transition is observed which is to a charge-ordered state only for certain $x$. On further cooling the material passes to an antiferromagnetic ground state with Neel temperature $T_N$ that depends on $x$. For $0.5 \leq x \leq 0.9$ the structural transformation occurs at the same temperature as the magnetic transition.

Overall, the neutron diffraction patterns were explained by considering four phase boundaries for which La$_{1-x}$Ca$_x$MnO$_3$ forms a distinct phase: the CE phase at $x = 0.5 - 0.55$; the charge-ordered phase at $x = 2/3$, the monoclinic and C-type magnetic structure at $x = 0.80 - 0.85$ and the G-type magnetic structure at $x = 1$. Between these phase boundaries the magnetic reflections suggest the existence of mixed compounds containing both phases of the adjacent phase boundaries in a ratio determined by the lever rule.

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The prototypical La$_{1-x}$Ca$_x$MnO$_3$ compound has been first studied experimentally with neutron diffraction by Wollan and Koehler and theoretically by Goudenough-Wollan and Koehler in the middle of 1950’s. In the last decade perovskite manganites have attracted (for some recent reviews see Ref. 3 and the references therein) significant research interest. Several works have been published on the phase diagram (or its parts) of La$_{1-x}$Ca$_x$MnO$_3$ compounds as function of carrier doping with emphasis around $x \sim 1/3$, where the maximum colossal magnetoresistance (CMR) effect has been observed (mainly due to its technological relevance). In the $x \geq 0.5$ regime where the charge/orbital ordering phenomenon appears, less studies have been devoted.

The richness of the phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ is the result of interplay between spin, charge and lattice degrees of freedom. For $0 \leq x \leq 0.21$ the system evolves from the antiferromagnetic ($x = 0$) to canted magnetic state and near $x \sim 0.2$ towards the insulating ferromagnetic state. For the range $0.21 < x < 0.5$, a ferromagnetic metallic ground state occurs that undergoes a coincident metal-to-insulator and FM-to-paramagnetic transformation on the temperature scale $150 - 250$ K. In the $0.5 \leq x \leq 0.9$ region, the system is not well studied except for some particular $x$. Up till now two distinct phases were revealed: $x = 1/2$ and $x = 2/3$. At half-doping ($x = 1/2$), the material undergoes a phase transition from paramagnetic (insulating) to ferrromagnetic-metallic (FM) phase at $T_c \approx 234$ K and upon further cooling passes to an antiferromagnetic-insulating (AFM) phase at $T_N = 163$ K. The antiferromagnetic phase presents charge and spin ordering, the CE-type structure, where real space ordering of Mn$^{3+}$ and Mn$^{4+}$ takes place. The basic characteristic of the $x = 1/2$ phase, at low temperatures, is the one after the other ordering of the Mn$^{3+}$ and Mn$^{4+}$ ions along the $c$ axis. The propagation vector $k = (1/2, 0, 0)$. The magnetic structure is a consequence of the structural superstructure.

For $x = 2/3$, below $T_{CO} \approx 260$ K the room temperature phase transforms into a charge-ordered low-temperature orthorhombic phase with space group $Pnma$, but with a tripled unit cell ($a_{CO} = 3a_0$, $b_{CO} = b_0$ and $c_{CO} = c_0$). In addition to the charge ordering, the $x = 2/3$ compound displays a non-collinear antiferromagnetic structure with the $a$ lattice parameter being tripled and the $c$ lattice parameter being doubled with respect to the average crystallographic unit cell $Pnma$ setting. The crystallographic structure below the charge-ordering temperature is characterized by ordering of the $d_{2z}$ orbitals of the Jahn-Teller-distorted Mn$^{3+}$O$_6$ octahedra in the orthorhombic $ac$ plane and the appearance of superlattice peaks in the x-ray patterns which corresponds to the tripling of the $a$ axis lattice parameter. The refinement revealed ordering of the Mn$^{3+}$ cations in sites as far apart as possible in the $ac$ plane. The Jahn-Teller distortion and Coulomb interaction are present, whereas for $0 < x < 1$ regime both ferrmagnetic and antiferromagnetic interactions are present, whereas for $x = 1$ CoO$_3$ display the G-type antiferromagnetic structure.

The charge and orbital ordering can be explained if one considers a delicate balance among two or more competing interactions such as Hund’s rule coupling, Jahn-Teller distortion and Coulomb interaction. The CE-state stabilization is induced by the kinetic energy of the $e_g$ electron, whose motion is restricted by the $t_{2g}$-spin alignment through the double-exchange mechanism.

In the intermediate doping range $1/2 < x < 2/3$ the situation is not so clear. The only available information is from high resolution electron diffraction lattice images which show that charge ordering appears as proper mixtures of the two adjacent distinct commensurate configurations according to the lever rule. In addition, the minority phase is not phase-separated into a sizeable area but instead, appears as
TABLE I: Refined unit cell parameters (Å), fractional atomic positions, anisotropic (for oxygen atoms) $b_{ij} \times 10^4$ (Å$^2$) and isotropic thermal Debye-Waller factors, and reliability factors derived from neutron diffraction data of La$_{1-x}$Ca$_x$MnO$_3$ samples at $T = 300$ K ($x = 0.5, 0.55, 0.6, 0.63, 0.72, 0.75$ and $0.9$). The space group $Pnma$ (No.62) was used for all samples. La, Ca and O(1) occupy the 4c ($x, 1/4, z$) site, Mn the 4a (0, 0, 0) site and O(2) the general 8d site. The numbers in parentheses are estimated standard deviations referring to the last significant digit.

| $x$ | $0.5$ | $0.55$ | $0.6$ | $0.63$ | $0.69$ | $0.72$ | $0.75$ | $0.9$ |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|
| $a$ | 5.4211(3) | 5.4117(2) | 5.4007(3) | 5.3818(2) | 5.3729(3) | 5.3628(4) | 5.3553(5) | 5.3082(1) |
| $b$ | 7.6446(4) | 7.6154(2) | 7.5916(3) | 7.5683(2) | 7.5612(2) | 7.5559(3) | 7.5479(5) | 7.4984(2) |
| $c$ | 5.4352(4) | 5.4195(2) | 5.4073(3) | 5.3883(2) | 5.3756(3) | 5.3634(4) | 5.3522(5) | 5.3004(1) |
| $\alpha_x$ | 1.87(1) | 1.83(2) | 1.78(3) | 1.74(2) | 1.72(3) | 1.69(4) | 1.65(5) | 1.60(6) |
| $\beta_x$ | 0.0305(3) | 0.0306(2) | 0.0310(2) | 0.0313(1) | 0.0310(2) | 0.0310(3) | 0.0310(4) | 0.0310(5) |
| $B_{0.7}$ | 0.0626(8) | 0.06128(56) | 0.0606(6) | 0.0607(5) | 0.0620(5) | 0.0613(8) | 0.0608(9) | 0.0621(1) |
| $B_{1.6}$ | 91(9) | 78(5) | 81(6) | 81(6) | 81(6) | 81(6) | 81(6) | 81(6) |
| $B_{2.2}$ | 12(6) | 31(4) | 30(4) | 13(3) | 10(3) | 3(3) | 0(5) | 31(9) |
| $B_{3.3}$ | 91(9) | 78(6) | 81(6) | 81(6) | 81(6) | 81(6) | 81(6) | 81(6) |
| $R_p$ | 5.19 | 4.84 | 4.64 | 4.81 | 4.91 | 4.92 | 5.47 | 5.77 |
| $R_{wpp}$ | 6.76 | 6.22 | 6.42 | 6.34 | 6.36 | 6.37 | 6.98 | 8.11 |
| $R_{wp}$ | 4.74 | 4.16 | 4.48 | 3.84 | 3.99 | 4.17 | 3.91 | 3.5 |
| $\chi^2$ | 2.03 | 2.22 | 2.06 | 2.72 | 2.54 | 2.33 | 3.19 | 5.35 |
| $R_B$ | 6.44 | 4.55 | 4.62 | 4.87 | 4.82 | 4.98 | 4.69 | 3.85 |

Incoherent stacking-fault defects in the otherwise perfect majority phase. Above $x \approx 0.8$ a distinct monoclinic phase has been observed with two Mn sites which display orbital ordering but no charge ordering. It is therefore of interest to examine and elucidate the intermediate compositions.

In the present paper using neutron diffraction and magnetization data we investigated the low temperature phase diagram of the La$_{1-x}$Ca$_x$MnO$_3$ compound for $0.5 \leq x \leq 0.9$. The main result is that, in this doping range, La$_{1-x}$Ca$_x$MnO$_3$ is a distinct phase only for certain $x$ ($0.5 - 0.55$, $x = 2/3$ and $x = 0.80 - 0.85$) and for the intermediate Ca contents is a mixture of the two adjacent boundaries. La$_{1-x}$Ca$_x$MnO$_3$ samples with $0.5 \leq x \leq 0.9$ 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 at temperatures up to 1400°C for several days with intermediate grindings. Finally, the samples were 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 $\lambda = 2.44$Å(from the (002) reflection of a pyrolytic graphite monochromator). For crystal structure refinement, data were collected on the E9 diffractometer with wavelengths $\lambda = 1.798$ and 1.589Å(from the (511) and (311) reflections of a vertically focusing Ge monochromator), with collimation $\alpha_1 = 10^\circ$ (in pile collimator), $\alpha_2 = 20^\circ$ (second collimator after monochromator) and $64 \times 10^\circ$ collimators in front of 64 °He single detector tubes. The powdered samples were placed in a cylindrical vanadium can ($D = 8$ mm) which was mounted in an ILL orange cryostat. DC magnetization measurements were performed in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

The structural parameters for all samples at $T = 300$ K were refined using the Rietveld method and the FULLPROF program. All refinements were carried out in the $Pnma$ space group. In the final stage of the refinement the thermal parameters for the oxygen ions were allowed to be anisotropic. The final structural parameters for all samples are listed in Table. As an example, figure shows the refined pattern for $x = 0.75$ at $T = 300$ K. In figure (a) we plot the variation of lattice parameters as a function of $x$. The cell parameters for...
the $x = 0.5$ sample follow the inequality $c > a > b/\sqrt{2}$ which is characteristic of a tolerance factor $t < 0.9$. As $x$ increases, the lattice parameters $a$ and $c$ decrease almost linearly and with the same slope. The $b$ length decreases also but the $b(x)/\sqrt{2}$ curve displays positive curvature and at $x \sim 0.8$ merges with the $a(x)$ and $c(x)$ curves. For larger $x$ all lattice parameters continue to decrease with nearly equal slopes. In addition, even though the difference between $a$ and $c$ is very small, it shows that close to $x = 0.8$ a change in the inequality relation of the cell parameters occurs and $a > c > b/\sqrt{2}$.

Fig. 2(b) depicts the variation of the individual, as well as the linearly interpolated Mn-O bond lengths, on $x$. Since all the samples are above the charge ordering temperature one can expect that the oxygen environment around manganese, in Ca substituted samples, acts like a linearly interpolated average of two end members $x = 0$ and 1 (solid lines in Fig. 2(b)). However, our data, clearly show that individual Mn-O bonds do not follow the linearly interpolated average. Furthermore, at certain calcium contain the bond lengths vs $x$ curves change slope abruptly. These $x$'s are related with $x = 2/3$ and 0.85 where phase boundaries occur in the La$_{1-x}$Ca$_x$MnO$_3$ phase diagram (vide infra). It is remarkable that the long bond length of Mn-O$_2$ (which corresponds to Jahn-Teller distortion) is far below the expected value for linearly interpolated of the end members ($d$(Mn – O$_2$) = 2.17(1 – $x$) + 1.90$x$). On the other hand the second Mn-O$_2$ bond length is larger than the linearly interpolated one. Finally the Mn-O$_1$ bond length follows the interpolated value. It is logical one to rise the question, what is the explanation for such a behavior? As has been noticed by Radaelli et al. a small coherent Jahn-Teller distortion is not incompatible with the large total distortion, provided that the largest part of it cancels upon application of the space group symmetry operators. The Jahn-Teller distortion at $T = 300$ K must be truly incoherent, either through static or dynamic disorder.

Figure 3 shows the temperature variation of the magnetic moment under a magnetic field of 1 kOe for samples with $x = 0.55, 0.6, 0.63, 0.69, 0.75$ and $0.9$ as a function of temperature. The measurement for $x = 0.55$ displays all the characteristics of the $x = 0.5$ sample.
Namely, the $m(T)$-curve shows the well known (for the CE structure) hysteretic behavior at $T_N$ which characterizes a first-order transition. The measurement for $x = 0.6$ reveals remarkable changes with respect to the samples that display the CE structure. The peak at high temperatures is related to a structural transition due to charge ordering and not to the appearance of ferromagnetic interactions. At lower temperatures a small anomaly in the $m(T)$ curves ($x = 0.6 - 0.69$) marks the antiferromagnetic ordering ($T_N$), in complete agreement with the thermal scans of neutron diffraction data (see below). For $0.55 < x < 0.63$ the heating and cooling $m(T)$-curves display a small hysteresis close to the $T_N$. Probably this hysteresis is a consequence of the mixed character of the sample (we note that at $T = 300$ K these samples are single phase material). As the calcium content is further increased the hysteresis and the shoulder at $T_N$ are further reduced. The neutron diffraction data show that for $0.75 \leq x \leq 0.85$ the temperature at which additional (antiferromagnetic) peaks appear in the neutron diffraction patterns is shifted towards the temperature at which the $m(T)$ curves display a peak. For $x = 0.75$ the structural and the magnetic transition occur with a temperature difference of 20 K and for $0.8 \leq x \leq 0.85$ the structural transition (a monoclinic distortion) coincides with the magnetic transition. Finally, for the $x = 0.9$ sample the $m(T)$-curve shows a variation characteristic of a ferromagnetic phase. From this measurement we can not exclude an antiferromagnetic component since its contribution to the bulk moment will be smaller by orders of magnitude.

Figure 3 shows the neutron diffraction patterns (NDP) at $T = 2$ K for all the samples. The pattern for $x = 0.5$ displays the classical antiferromagnetic CE structure which can be described with the propagation vectors $k_C = [1/2, 0, 1/2]$ and $k_E = [0, 0, 1/2]$ for Mn$^{3+}$ and Mn$^{4+}$ sublattices respectively. The symmetry and the initial orientation of the moments for the refinement of this structure were taken from the data reported in Ref. 13. In the CE structure Mn$^{3+}$ and Mn$^{4+}$ are ordered and are located in two crystallographically independent sites. The ordered magnetic moments at $T = 1.6$ K for the two sublattices were found to be $\mathbf{m}$(Mn$^{3+}$) = (1.01, 0.28) $\mu_B$ and $\mathbf{m}$(Mn$^{4+}$) = (0, 0, 2.57) $\mu_B$, respectively. As also noted in Ref. 14, the magnetic reflections associated with the Mn$^{3+}$ cations are considerably broader than those generated by the Mn$^{4+}$ sublattice. This behavior has been convincingly explained in this paper by assuming the existence of twinning generated by an operation that leaves the Mn$^{4+}$ magnetic sublattice unperturbed while it decreases the size of the Mn$^{3+}$ magnetic domains.

The pattern for the $x = 0.55$ sample continues to display the basic characteristics of the CE structure, except...
for the significant broadening of the reflections of the E- type magnetic structure. In addition the \((1, 1, 1/2)\) peak moves to lower angles with respect to the position expected from the crystal structure. These results may be explained as due to the smaller size of the \(\text{Mn}^{3+}\) domains. As the \(\text{Mn}^{3+}\) domains decrease in size with increasing \(x\), the relative fraction of surface spins increases and so does the spin disorder in these domains. Thus, the apparent \(\text{Mn}^{3+}\) magnetic moment is lowered. Further substitution of La for Ca in the CE structure dilutes the \(\text{Mn}^{3+}\) sublattice with \(\text{Mn}^{4+}\) ions. This dilution is manifested by broadening and shifting of the corresponding peaks. Incommensurabilities, which are doping dependent, may be an indication that the antiferromagnetic ground state is in the itinerant limit. By considering AFM in the itinerant limit and its competition with CO and ferromagnetism, one can understand the softness of the insulating state filling to a magnetic field.

As the \(\text{Mn}^{3+}\) charge-ordered model is of interest to note that the appearance of the magnetic peaks is not characteristic of a second order magnetic transition. Rather these broad peaks are reminiscent of short range order. It might be the case that, in this regime, the competition between the CE- and 2/3- structure charge-ordering imposes this complicated behavior. Close to \(x = 2/3\) (e.g. \(x = 0.63\) and \(x = 0.69\) samples) the NDP are characteristic of the antiferromagnetic Wigner crystal charge-ordered structure. All the magnetic reflections can be indexed with two propagation vectors: \(k_{2/3} = [1/3, 0, 1/2]\) and \(k_{C} = [0, 0, 1/2]\).

Small intensity peaks of the C-type magnetic structure are also present, but these peaks should be eliminated exactly at \(x = 2/3\) or after prolonged annealing that allows the preparation of a homogeneous sample. This phase is stable in a region around \(x = 2/3\). A Rietveld refinement of the magnetic and crystal structure at \(T = 2\) K for \(x = 0.63\) sample using the Wigner crystal charge-ordered model gave ordered-magnetic moment for two sublattices \(\mathbf{m}(\text{Mn}^{3+}) = (1.99, 0, 1.24)\ \mu_{B}\) and \(\mathbf{m}(\text{Mn}^{4+}) = (1.87, 0, 1.58)\ \mu_{B}\), respectively.

For \(x > 2/3\) the \(\text{Mn}^{3+}\) sublattice is further diluted, thereby leading to the development of the C-type magnetic structure. Magnetic peaks which correspond to the propagation vector \(k_{3/4} = [1/4, 0, 1/2]\) appear. At \(x = 0.75\) one can expect a new charge-ordered phase with \(a = 4a_{Pnma}\). Our NDP for this calcium concentration revealed coexistence of magnetic peaks corresponding to the \(x = 2/3\) phase as well as to the propagation vectors \(k_{3/4}\) and \(k_{C}\). In order to check if prolonged annealing does stabilize a phase with \(a = 4a_{Pnma}\), two samples were measured. The first was annealed at 1400°C for 7 days and the second for 14 days. Even though the intensity of the \(k_{3/4}\) peaks increases, the peaks remain broad. On the other hand, the \(k_{3/4}\) peaks reduce in intensity but do not disappear. Remarkable is the disappearance of the magnetic peaks which correspond to the propagation vector \(k_{2/3}\) around 150 K. The corresponding peaks of \(k_{3/4}\) are disappeared at higher temperature, whereas those of \(k_{C}\) in the interval 170-190 K (see Fig. 3(b)).

For \(0.8 \leq x \leq 0.85\) a monoclinic distortion and antiferromagnetic C-type long range order are observed. Figure 3(a) depicts the thermal evolution of the NDPs for \(x = 0.9\). The NDPs show a mixed magnetic structure comprising both C- and G-type magnetic peaks. The presence of two propagation vectors may imply that the magnetic structure is non-collinear. The variation

![Neutron Diffraction Patterns](image-url)
FIG. 6: (a) Neutron diffraction patterns of La$_{0.1}$Ca$_{0.9}$MnO$_3$ for $2 \leq T \leq 180$ K. (b) Temperature variation of the lattice parameters. (c) Temperature variation of the ordered magnetic moment of the C- and G-type magnetic structures.

FIG. 7: Phase diagram of the La$_{1-x}$Ca$_x$MnO$_3$ compound in the high Ca doping region $x = 0.5 - 0.9$. 
of the magnetization shows ferromagnetic behavior with $T_c \sim 110$ K. We note that the peaks corresponding to the C and G magnetic structures do not disappear simultaneously. The C-type peaks are present at $T = 120$ K, whereas the G-type peaks disappear in agreement with the magnetization measurement. No anomaly was observed in the magnetization measurements since the large ferromagnetic signal should mask the much smaller antiferromagnetic one. The ferromagnetic moment is favorable for the non-collinear magnetic structure. Regarding the crystal structure, the monoclinic distortion observed for the samples $x = 0.8$ and $x = 0.85$ disappears or is below the resolution limit of the instrument. At the temperature where the magnetic peaks appear, the $b$-axis decreases and $a$-axis increases, while the $c$-axis remains nearly constant (see fig. 3(b)). Rietveld refinement at $T = 1.6$ K gave ordered magnetic moments $m_C = (1.81(5), 0, 0)$ and $m_G = (2.34(5), 0.3(1)) \mu_B$ for the C- and G-type magnetic structures, respectively. Figure 6(c) shows the temperature variation of the $m_C$ and $m_G$ ordered moments for $x = 0.9$.

In Fig. 7 we compiled both the magnetization and neutron data to produce a phase diagram for the La$_{1-x}$Ca$_x$MnO$_3$ system in the doping region $0.5 \leq x \leq 0.9$. This is the main result of our work. On increasing the Ca content above the $x \sim 0.5$ boundary, the system retains the CE-structure even though the Mn$^{3+}$ sublattice is diluted with Mn$^{4+}$ ions. In the doping range $0.55 < x < 2/3$ the CE and 2/3 phases coexist due to the competition between the forces which stabilize these phases. It is only when the Mn$^{3+}$/Mn$^{4+}$ ratio is a certain rational number that charge-ordering occurs. Otherwise, the system consists of a mixture of the two phases according to the lever rule. Another clear phase boundary occurs in the vicinity of $x = 0.8$. However, this phase does not clearly display charge-ordering. In the regime $2/3 < x < 0.8$ there is coexistence of the two phases with an additional complication due to the fluctuations which tend to stabilize $x = 3/4$ charge-ordered state. Finally, for $0.85 < x < 1$ the C- and G-type magnetic structures coexist (G is the magnetic structure adopted by the CaMnO$_3$).

The temperature where the structural transition occurs seems to follow the lever rule (fig. 7), i.e. it increases in the region $0.55 < x < 2/3$ towards the value $T_{CO}(x = 2/3) \approx 270$ K. The corresponding Neel temperature (we must not forget that in this region we have a mixture) is approximately constant or decreases slightly. Perhaps this is due to the fact that the $T_N$ temperatures of the CE and 2/3-structures are approximately equal. Similarly, the reduction of the structural transition temperature can be explained with the lever rule, in agreement with the high resolution electron diffraction data. At the region where only the C-structure is present the structural and the magnetic transition occur concurrently. The temperature where the magnetic peaks appear ($T_N$) increases approaching the value of the $x = 0.8$ sample. In several previous works $T_N$ was shown to decrease monotonically up to $x = 0.9$, in contrast with our neutron data.

In conclusion, we studied the low temperature phase diagram of the La$_{1-x}$Ca$_x$MnO$_3$ compound for $0.5 \leq x \leq 0.9$ using elastic neutron diffraction data and magnetic measurements. The neutron diffraction patterns can be consistently explained by considering the existence of four phase boundaries $x = 0.5 - 0.55$, $x = 2/3$, $x = 0.80 - 0.85$ and $x = 1$ at which the material forms a distinct crystallographic and magnetic phase. At the intermediate $x$ it consists of a mixture of the two adjacent boundaries according to the lever rule. The variation of the $T_N$ and of the structural transition temperature with the Ca doping content can be constructed by applying the lever rule. A final interesting result is that for $x = 0.80 - 0.90$ the magnetic and the structural transition occur simultaneously.

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