Charge, Orbital and Magnetic Order in $Nd_{0.5}Ca_{0.5}MnO_3$

F. Millange$^1$, S. de Brion$^2$, G. Chouteau$^2$

$^1$ CRISMAT-ISMRA
CNRS and Université de Caen
6, boulevard du Maréchal Juin
14050 Caen - France

present address: Inorganic Chemistry Laboratory
South Parks - Oxford OX1 3QR, England.

$^2$Grenoble High Magnetic Field Laboratory
BP 166 - 38042 Grenoble cedex 9- France

* corresponding author
Abstract

In the manganite $Nd_{0.5}Ca_{0.5}MnO_3$, charge ordering occurs at much higher temperature than the antiferromagnetic order ($T_{CO} = 250K$, $T_N = 160K$). The magnetic behavior of the phase $T_N < T < T_{CO}$ is puzzling: its magnetization and susceptibility are typical of an antiferromagnet while no magnetic order is detected by neutron diffraction. We have undertaken an extensive study of the crystallographic, electric and magnetic properties of $Nd_{0.5}Ca_{0.5}MnO_3$ and established its phase diagram as a function of temperature and magnetic field. The charge disordered, paramagnetic phase above $T_{CO}$ present ferromagnetic correlations. An antiferromagnetic CE phase prevails below $T_N$, with complete charge and orbital ordering. In the intermediate temperature range, charge ordering occurs while orbital ordering sets in progressively, with no magnetic order. Strong magnetic fields destroy the charge ordered phases in a first order transition towards a ferromagnetic state.
I. INTRODUCTION

The manganites $L_{1-x}M_xMnO_3$, where $L$ is a trivalent rare earth and $M$ a divalent alkaline earth element, present astonishing properties due to the interplay of magnetism, electric transport and crystallographic distortion. Much interest has been focused on the hole doped ferromagnetic phase ($x \simeq 0.3$) which exhibits colossal magnetoresistance [1]. At fractional doping level, another mechanism is superimposed: charge ordering between $Mn^{3+}$ and $Mn^{4+}$ ions takes place [2] [3] [4] [5]. The crystallographic and magnetic environment is then strongly modified. For instance, $Nd_{0.5}Sr_{0.5}MnO_3$ [3] [5] is ferromagnetic and metallic below 245K. At 160K, the charge order transition occurs and the system becomes antiferromagnetic and insulating. Applying a strong magnetic field restores the ferromagnetic order together with the metallic conductivity.

However these properties depend crucially on the local lattice distortion and the mismatch between the rare earth and the alkaline element [6] [7]. In these perovskite structure, it is convenient to define the tolerance factor $t = (r_{L,M} + r_O)/\sqrt{2} (r_{Mn} + r_O)$ where $r_{L,M}$, $r_{Mn}$ and $r_O$ are the average ionic radii of the trivalent rare earth and divalent alkaline earth site, manganese site and oxygen site respectively. It describes the distortion of the perovskite structure. This distortion modifies the strength of the different magnetic interactions present in these systems. The double exchange mechanism [8] couples the itinerant 3$d$ $e_g$ electrons of $Mn^{3+}$ with the localized 3$d$t$_{2g}$ spins of the $Mn^{4+}$ ions. It favors ferromagnetism together with metallic conductivity. It depends on the number of $e_g$ electrons as well as the bond angle Mn-O-Mn governed by the lattice distortion. On the other hand, the superexchange interaction between manganese ions favors antiferromagnetic order with localized spins with then insulating electric properties. Decreasing the ionic radius of the L and M site modifies the bond angle Mn-O-Mn. The ferromagnetic ordering interaction is then reduced [3]. The bandwidth of the $e_g$ electron becomes narrower. Eventually, the system becomes insulating and lost its ferromagnetic order.

Additionally, for $x = 0.5$, charge ordering will tend to localize the spins and destabilize...
the ferromagnetic order. This is what has been observed in $Nd_{0.5}Sr_{0.5}MnO_3$ [3] and in $Pr_{0.5}Sr_{0.5}MnO_3$ [2] where the tolerance factor is close to 0.95. The ferromagnetic, metallic order, established below $T_C \approx 250K$, is destroyed when charge ordering sets in at $T_{CO} \approx 150K$, and the system becomes antiferromagnetic and insulating ($T_N = T_{CO}$).

For smaller tolerance factor, the magnetic phase diagram is not so clear. In $Pr_{0.5}Ca_{0.5}MnO_3$ [3, 10], with $t = 0.933$, or in $Sm_{0.5}Ca_{0.5}MnO_3$ ($t = 0.924$) [4], the charge order state occurs at higher temperature ($T_{CO} \approx 250K$) so that no ferromagnetic order is established in zero magnetic field. Antiferromagnetism is observed only at lower temperature ($T_N \approx 150K < T_{CO}$).

Surprisingly, the magnetic susceptibility presents a huge peak at $T_{CO}$, as observed for a long range antiferromagnetic order, and none at $T_N$. Such a behavior is very sensitive to stoichiometry. In $Pr_{0.6}Ca_{0.4}MnO_3$ [3, 11], as well as in $Nd_{0.6}Ca_{0.4}MnO_3$ [12], the anomaly at $T_{CO}$ persists while the signature of $T_N$ is quite visible. What is the exact nature of the phase when $T_N < T < T_{CO}$? What is the mechanism responsible for the susceptibility anomaly at $T_{CO}$? To answer these questions, we have focused on the compound $Nd_{0.5}Ca_{0.5}MnO_3$ for which $t = 0.930$. We have undertaken an extensive study of its crystallographic, electric and magnetic properties using neutron diffraction, electric transport, magnetic susceptibility and high field magnetization measurements.

II. EXPERIMENTS

The powdered sample was prepared by solid state reaction from the component oxides in appropriate ratios. The reagents were intimately mixed in an agate mortar and heated in air at $900^\circ C$ for 12 hours to allow decarbonation to take place. This powder was fired at $1200^\circ C$ for 12 hours. Final firing was performed at $1500^\circ C$ for five days with intermediate grinding to ensure homogeneity. Phase purity was checked by X ray diffraction using a Phillips diffractometer with Cu K$_\alpha$ radiation.

The phase $Nd_{0.5}Ca_{0.5}MnO_3$ was subsequently registered on the high-resolution diffract-
tometer D2b at the Institut Laue Langevin using a wavelength of $\lambda = 1.5938\,\text{Å}$ at room temperature and 1.5 K. The sample was contained in a vanadium can. The high-flux powder diffractometer CRG-CNRS D1b was used to investigate the thermal dependence of the magnetic structure in the temperature range $1.5\,\text{K} - 293\,\text{K}$. Thanks to the position sensitive detector covering $80^\circ(2\theta)$ and the high neutron flux available at the $2.52\,\text{Å}$ wavelength, a neutron diffraction pattern has been measured every 6 Kelvin. The nuclear and magnetic refinement were performed using the profile fitting program Fullprof [13] ($b_{\text{Mn}} = -0.373.10^{-12}\text{cm}$, 

$b_{\text{O}} = 0.580.10^{-12}\text{cm}$, $b_{\text{Nd}} = 0.769.10^{-12}\text{cm}$, $b_{\text{Ca}} = 0.470.10^{-12}\text{cm}$).

Magnetic susceptibility measurements were made with a SQUID magnetometer (MPMS Quantum Design) in the temperature range 4K-350K. These D.C. susceptibility measurements were carried out at low field (10 mT) with increasing temperature after the samples were either zero field cooled (ZFC) or field cooled (FC). High temperature susceptibility measurements were also taken up to 800K using a faraday balance. High field magnetization measurements were performed, up to 22T, with a conventional extraction set-up, in the temperature range 4K-300K.

The electric resistivity was measured between 5 K and 600 K, using a standard four points method, on a bar with typical dimensions $0.2 \times 0.2 \times 1\text{cm}^3$. Magnetoresistance measurements were performed with magnetic fields up to 7T, the temperature ranging from 5 K to 400 K.

III. RESULTS

A. Neutrons

The powder neutron diffraction pattern of $Nd_{0.5}Ca_{0.5}MnO_3$, collected at room temperature in the paramagnetic domain, exhibits the orthorhombic $GdFeO_3$ structure ($a \approx a_p\sqrt{2}$, $b \approx 2a_p$, $c \approx a_p\sqrt{2}$). Refinements of the room temperature neutron diffraction patterns, carried out in the space group $Pnma$ attest the validity of the structure resolution. The
data were first analyzed with a ‘whole pattern fitting’ algorithm in order to determine accurately the profile shape function, background and cell parameters. This preliminary study provided a good estimate of the $R_{wp}$ and $\chi^2$ that could be reached during the structure refinement. This whole pattern fitting led to an agreement factor $R_{wp} = 4.48\%$ and $\chi^2 = 1.42$. The refinement was undertaken with the room temperature neutron diffraction pattern, a temperature for which the magnetic measurements showed a paramagnetic behavior (see the magnetic properties section). 235 Bragg peaks were used to refine 7 positional parameters and 4 isotropic temperature factors. The refinement converged to give an agreement factor $R_{wp} = 4.84\%$ and $\chi^2 = 1.71$. Observed, calculated and difference diffraction profiles are shown in Figure 1. A Jahn-Teller (J-T) distortion of the $Q_2$ type (antiferrodistorsive), that displaces the basal plane oxygen atoms from their ideal positions, has been proposed to be responsible for the insulating state. This distortion does not change the lattice symmetry ($Pnma$) but modifies the cell deformation in such a way that $b/\sqrt{2} \leq c \leq a$ (the $O'$-type structure). Thus, the resulting Mn-O bond lengths of 1.943 Å and 1.948 Å (basal plane) and 1.936 Å (apical distance) at room temperature are at the origin of a small gap between the J-T split Mn $e_g$ bands ($d_{x^2-y^2}$ and $d_{z^2}$).

On cooling the specimen $Nd_{0.5}Ca_{0.5}MnO_3$ below 250 K, very weak extra reflections appear on the electron microdiffraction patterns [14]. The patterns can only be indexed by doubling the $a$ lattice parameter. However, the extra reflections are too weak to determine the point group from electron microdiffraction patterns and from convergent beam electron diffraction patterns. Therefore, subsequent refinements based on neutron diffraction data were carried out in the higher symmetry $Pnma$ space group, characteristic of the structure above the transition. It should be clear that this procedure will yield only a structure averaged over the symmetry operators of the $Pnma$ space group. Refinements of a $Pnma$ model lead to large displacement parameters of the oxygen atoms indicative of disorder and/or subtle distortions not taken into account by an orthorhombic model. The corresponding $Nd_{0.5}Ca_{0.5}MnO_3$ structural parameters, selected bond distances and angles at room temperature and 1.5 K are reported in Table 1. The most significant difference
between the room temperature and the low temperature structures is in the Mn-O bond lengths. At room temperature, the octahedral coordination of manganese with oxygen is almost undistorted, with six approximately equal Mn-O distances. At low temperature, the two $Mn - O_1$ distances (along the b axis) become shorter than the four $Mn - O_2$ distances in the a-c plane, implying a J-T distortion of the 'apically compressed' type as previously reported by Radaelli et al. [15] in $La_{0.5}Ca_{0.5}MnO_3$. The mean distortion in the $MnO_6$ octahedra $\Delta_d$ is increased by a factor of 20 as the temperature decreases from room temperature to low temperature. These results clearly demonstrate that there is a close link between the lattice parameters and the presence of the J-T distorted $Mn^{3+}O_6$ octahedra with the $d_{z^2}$ orbital oriented in the a-c plane.

The high-flux powder diffractometer D1b was first used to investigate the thermal dependence of the orthorhombic cell parameters in the temperature range of 1.5 K-293 K (Figure 3). One observes that a and c parameters increase as the temperature is lowered from $T_{CO} = 250K$ to $T = 160K$ accompanied by a significant decrease in the b parameter. Our results demonstrate that the charge ordered state is progressively established from $T_{CO} = 250K$ to $T = 160K$.

The magnetic reflections in the low-temperature neutron powder diffraction pattern have been indexed on the basis of $(a \approx a_p \sqrt{2}, b \approx 2a_p, c \approx a_p \sqrt{2})$ unit cell, previously reported by Wollan and Koehler [16]. The magnetic structure of $Nd_{0.5}Ca_{0.5}MnO_3$, known as CE-type (Figure 4), is quite complex: it entails a quadrupling of the volume of the original orthorhombic unit cell and consists of two magnetic sublattices with independent propagation vectors. This observation, associated with the fact that $Nd_{0.5}Ca_{0.5}MnO_3$ is an insulator (see electrical properties below), has confirmed the hypothesis, first formulated by Goodenough [17] and developed by others [18], that the two sublattices result from charge ordering between $Mn^{3+}$ and $Mn^{4+}$. In Goodenough’s model, charge ordering is accompanied by orbital ordering forming ferromagnetic zig-zag chains in the a-c plane ($d_{z^2} Mn^{3+}$ orbitals associated with the long $Mn^{3+} - O$ bonds in the J-T distorted $Mn^{3+}O_6$ octahedra). These ferromagnetic chains are connected antiferromagnetically each others in the a-c plane and along the
The magnetic structures of the two sublattices have different propagation vectors: \( \vec{k}_1 = (0, 0, 1/2) \) for \( Mn^{3+} \) and \( \vec{k}_2 = (1/2, 0, 1/2) \) for \( Mn^{4+} \). Rietveld refinements of the low-temperature neutron powder diffraction pattern clearly indicate that the magnetic moments are oriented along the a-axis (Figure 4). The refined values of the magnetic moments at 2K are reported in Table 2 while their temperature variations are plotted in Figure 4. Above \( T_N = 160K \), this magnetic moment vanishes. It is worth noticing that the long range antiferromagnetic order is established only well below \( T_{CO} \). It is important to note here that \( T_N \) exactly coincides with the temperature below which the lattice parameters become constant (Figure 3).

### B. Electric properties

The electric resistivity \( \rho(T) \) is plotted in Figure 6. The compound remains insulating what ever the temperature. Below 50K, the resistivity is too high to be measured. Such an insulating state is in agreement with Goodenough predictions of the CE type antiferromagnetic state. The discontinuity around 250K corresponds to the charge order transition. Magnetic fields have little effects on the resistivity, up to 7 T at least. Above \( T_{CO} \), a model of small polaron describes correctly the temperature dependence:

\[
\rho(T) = \rho_0 + A T^{1.5} e^{(E/T)} \text{ with } \rho_0 = 1.76 \times 10^{-3} \text{ \Omega cm}, \quad A = 1.40 \times 10^{-8}, \quad E = 947K.
\]

At lower temperature, Below \( T_N \), a model of variable range hoping is more suitable: \( \rho(T) = A e^{(E/T)^{0.25}} \) with \( A = 1.84 \times 10^{-16}, \quad E = 3.4 \times 10^8 K \). In the intermediate temperature range, there is a gradual change from the polaronic behavior towards the variable range hopping behavior.

### C. Magnetic properties

The DC susceptibility \( \chi_{DC} \) is plotted in Figure 7 as a function of temperature. A pronounced peak is visible at 250K which corresponds to the charge ordering temperature \( T_{CO} \) established by neutron diffraction investigation. Below \( T_{CO} \), the susceptibility is reduced
suggesting the occurrence of antiferromagnetic correlations giving no long range order. On the other hand, no anomaly occurs at the antiferromagnetic ordering temperature $T_N$ determined by neutron diffraction analysis. The increase in $\chi_{DC}$ at low temperatures is attributed to $Nd^{3+}$ ions and will be discussed later.

We have also undertaken high temperature susceptibility measurements up to 800K using a Faraday balance. The susceptibility follows a Curie-Weiss law with a positive Curie Temperature $\theta_1 = 216K$ indicative of ferromagnetic interactions, (Figure 8). The Curie constant deduced from the linear part of the $\chi_{DC}(T)$ curve, (450 K <T <800 K), gives an effective moment $\mu_{eff} = 5.30\mu_B$. Assuming a rigid coupling of the moments of the $Nd^{3+}$, $Mn^{4+}$ and $Mn^{3+}$ ions, one should measure, with 0.5 $Nd^{3+}$, 0.5 $Mn^{4+}$ and 0.5 $Mn^{3+}$ ions per formula unit, $\mu_{eff}^{calc} = \sqrt{0.5.\mu_{eff}^2(Nd^{3+}) + 0.5.\mu_{eff}^2(Mn^{3+}) + 0.5.\mu_{eff}^2(Mn^{4+})}$. The following assumptions have been made: the electronic levels of $Nd^{3+}$, at high temperature, are well described by $g = \frac{8}{11}$, $J = \frac{9}{2}$, which leads to $\mu_{eff} = gJ(J+1)\mu_B = 3.62\mu_B$; for $Mn^{4+}$ and $Mn^{3+}$, the orbital momentum is quenched so that $S$ is the appropriate quantum number: $\mu_{eff} = gS(S+1)\mu_B$, with $g = 2$ and $S = \frac{3}{2}$ or 2, which leads to $\mu_{eff} = 3.87\mu_B$ for $Mn^{4+}$ and $\mu_{eff} = 4.90\mu_B$ for $Mn^{3+}$. This gives $\mu_{eff}^{calc} = 5.10\mu_B$, not far from the experimental value.

DC magnetization measurements were performed up to 22 Tesla. Typical curves are plotted in Figure 9, one taken above $T_{CO}$, two others between $T_{CO}$ and $T_N$ and the last one below $T_N$. From these data, it seems that the compound presents a magnetic order occurring at the same time as the charge order. A field induced transition, analogous to a spin flop transition, is clearly visible below $T_{CO}$. This transition is first order, that is, strongly hysteretic.

We have further analyzed the magnetization curves in terms of Brillouin function, above the "spin flop field", by plotting the magnetization $M$ as a function of $H_i/T$ where $H_i$ is the internal field: $H_i = H_a + H_m$, $H_a$ is the applied field and $H_m$ the molecular field due to the magnetic interactions, proportional to the magnetization. All the curves in the temperature range 290K-170K collapse on a single curve at high field with the following fitting parameters: the Curie temperature is $\theta_2 = 175K$ and the effective moment is 5.83$\mu_B$.  

It should be noted that this analysis is made in the temperature range where $\chi_{DC}$ slightly departs from the high temperature Curie-Weiss law, (Figure 8). This would indicate that the susceptibility could be described with two Curie-Weiss laws, one with $\theta_2 = 175K = T_N$, $\mu_{eff} = 5.83\mu_B$ for the temperature range 170K$\leqslant T < 290$K and for high magnetic fields and the other one with $\theta_1 = 210K \simeq T_{CO}$, $\mu_{eff} = 5.30\mu_B$ for $T > 400$K.

As the temperature is lowered, the influence of the neodymium ions becomes visible in the magnetic response of the compound: the susceptibility increases at low temperature while the magnetization does not saturate. It is however quite difficult to estimate exactly the neodymium contribution at these temperature because of crystal field effects on the Nd electronic level. For instance, in $NdGaO_3$ [19] which has a similar perovskite structure, the $J=9/2$ electronic level is split into 5 Kramer doublets separated by 137K, 133K, 363K and 183K so that only the fundamental level with effective spin 1/2 is occupied at low temperature. This will give a smaller effective moment and a strong deviation from a Curie law. This is exactly what is observed at low temperature in the magnetic susceptibility (see Figure 7).

IV. DISCUSSION

From the neutron diffraction and magnetization data, we can extract a phase diagram (Figure 10). The paramagnetic phase (P), above $T_{CO}$, is a Jahn-Teller distorted phase. It is an insulator with a thermally activated behavior. At low temperature, below $T_N$, an antiferromagnetic phase (AF-O) with complete charge and orbital ordering is present. Ferromagnetic zig-zag chains of $Mn^{3+}$ and $Mn^{4+}$ are formed in the a-c plane. The Jahn-Teller distortion of the $Mn-O_6$ octahedra has considerably increased. At the same time, the electrical resistivity reflects some kind of disorder: a variable range hopping regime prevails. In the intermediate temperature range , $Mn^{3+}$ and $Mn^{4+}$ are ordered, giving rise to a doubling of the a lattice parameter, while the orbital ordering is progressively established. It is clear that two different charge ordered phases are present: a charge ordered phase
with no long range magnetic order in the temperature range $T_N < T < T_{CO}$, and a long range antiferromagnetic phase with complete orbital ordering for $T < T_N$. Both phases have similar response to magnetic field: at low field, they are characterized by a small magnetic susceptibility. At higher field, both phases present a spin flop transition, with a first order character; the charge ordered state is then destroyed by the magnetic field and a ferromagnetic state prevails.

In Figure 11, we have plotted the magnetization of this ferromagnetic phase as a function of temperature, for two different fields: 15$T$ and 20$T$ deduced from the $M(H)$ curves. The maximum at $T_{CO}$ has been completely removed which confirms that it is associated with the charge ordering transition. We can distinguish two different contributions to the magnetization: one arises from the Neodymium ions, the other one from the manganese ions.

The Neodymium ions are paramagnetic (no magnetic order has been detected by neutron diffraction in this temperature range). Their magnetic moment is no longer described by $g = \frac{8}{11}$, $J = \frac{9}{2}$ as has been already mentioned. Using the experimental data on $NdGaO_3$ [19], we can estimate their contribution at 40K: $M(15T) \simeq 0.24\mu_B$ and $M(20T) \simeq 0.32\mu_B$ per formula unit. Experimentally, we get $M(15T) \simeq 3.6\mu_B$ and $M(20T) \simeq 3.8\mu_B$. The gap can therefore reasonably be attributed to the Neodymium ions, which leaves a value of $3.5\mu_B$ for the manganese ions: this is exactly the expected saturated magnetic moment for 0.5 $Mn^{4+}$ and 0.5 $Mn^{3+}$.

The ferromagnetic phase has then a conventional behavior: in the paramagnetic regime, a Curie Weiss law is observed with an effective moment $5.30\mu_B$ close to the theoretical one and with a Curie Temperature $\theta_1 = 216K$. The ordering temperature coincides with the Curie temperature $T_C \simeq \theta_1$. All these results suggests an isotropic ferromagnetic exchange interaction between each $Mn^{4+}$ and $Mn^{3+}$ ions, in agreement with the double exchange model. At low temperature, all the manganese magnetic moment are aligned with a net magnetization of $3.5\mu_B$. Around the magnetic transition, the system is best described by $\theta_2 = 175K$ and $\mu_{eff} = 5.83\mu_B$, revealing the presence of antiferromagnetic correlations.
The low field, charge ordered phase is much more unconventional: whereas magnetization measurements suggest that \( T_N = T_{CO} \), neutron diffraction measurements clearly demonstrate that the antiferromagnetic order is only established 100 K below \( T_{CO} \). A huge peak in the susceptibility is observed at \( T_{CO} \), as well as a jump in the magnetization as a function of field while no additional lines appear in the neutron diffraction spectra above \( T_N \).

We can reconcile all the experimental results as follows.

When lowering the temperature from room temperature, the susceptibility first increases due to the formation of a ferromagnetic phase. But this tendency to ferromagnetic order is destroyed by charge ordering which favors antiferromagnetism. The quenching of the double exchange interaction is responsible for the susceptibility peak at \( T_{CO} \) as was proposed already in \( [9] \). In the temperature range \( T_N < T < T_{CO} \), orbital ordering sets in progressively; it is only achieved around 160K where long range magnetic order is established. This is suggested by the temperature variation of the lattice parameters: as the temperature is lowered from \( T_{CO} \), they progressively decrease and remain constant only below \( T_N \). In this picture, when \( T_N < T < T_{CO} \), the manganese ions are charge ordered without complete orbital ordering. Several hypotheses remain.

The first one is that \( T_{CO} \) corresponds to a magnetic transition towards some unconventional magnetic order, such as modulated or helicoidal phase or non commensurate phase, \( T_{CO} \simeq T_{N1} \), and \( T_N \) corresponds to a commensurate magnetic order. There are some experimental evidences, in electron microscopy measurements, that the charge ordered state has a non commensurable structure in the temperature range \( T_N < T < T_{CO} \).

The second hypothesis is that it is not a long range magnetic order but rather fluctuations are present: ferromagnetic fluctuations above \( T_{CO} \) and increasing antiferromagnetic fluctuations together with decreasing ferromagnetic fluctuations below \( T_{CO} \), giving rise to the susceptibility peak at \( T_{CO} \). A similar behavior has been observed in \( Bi_{0.18}Ca_{0.82}MnO_3 \) \( [20] \): ferromagnetic fluctuations have been observed above the charge order transition \( T_{CO} \) but disappears at \( T_{CO} \) while antiferromagnetic correlations set in. A long range antiferro-
magnetic order was found at lower temperature.

A third hypothesis is that there is a mixture of the ferromagnetic phase and the charge ordered phase. Similar mixing of phases has been observed in $La_{0.5}Ca_{0.5}MnO_3$ using NMR [21]: antiferromagnetic and ferromagnetic domains are found to coexist at all temperatures below the first formation of charge ordered state.

The first hypothesis should be disregarded since no additional peak were observed in the high resolution neutron diffraction patterns. Besides, recent Electron Spin Resonance measurements on the same $Nd_{0.5}Ca_{0.5}MnO_3$ compound [22] are in favor of the second hypothesis: the charge ordered phase is characterized by strong magnetic fluctuations with no long range magnetic order.

V. CONCLUSIONS

Combining neutron diffraction, electric transport and magnetization measurements, we have obtained a detailed description of $Nd_{0.5}Ca_{0.5}MnO_3$ phase diagram.

We have shown that, in the compound $Nd_{0.5}Ca_{0.5}MnO_3$, the paramagnetic regime above $T_{CO} = 250K$ corresponds to the progressive establishment of a ferromagnetic phase with $T_C \simeq \theta_1 \simeq T_{CO}$.

From neutron diffraction experiments, a long range antiferromagnetic phase is observed only below $T_N = 160K$. Then the manganese ions form ferromagnetic zig-zag chains coupled antiferromagnetically (CE type of ordering). The Jahn-Teller distortion is greatly enhanced and complete orbital ordering is established. The compound remains insulating.

A more complicated phase exists between $T_N$ and $T_{CO}$. In this phase, orbital ordering sets in progressively. antiferromagnetic and ferromagnetic interactions compete. At low magnetic field, a non magnetic, insulating state prevails whereas at high magnetic field the ferromagnetic state is favored. The transition towards the ferromagnetic phase, from the non-magnetic as well as the magnetic charge ordered phase is strongly hysteretic revealing a first order type transition.
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VII. FIGURE AND TABLE CAPTIONS

Table 1: $Nd_{0.5}Ca_{0.5}MnO_3$ structural parameters at room temperature (RT) and 1.5K, as determined from Rietveld refinements based on neutron powder diffraction data.

Table 2: Refined magnetic moment components of the $Mn^{3+}$ and $Mn^{4+}$ sublattices, the site coordinates are expressed as fractions of the $(2a \times b \times 2c)$ magnetic cell.

Figure 1: Rietveld refinement plot of the neutron diffraction data at room temperature. The ticks are given for the nuclear structure peaks.

Figure 2: Rietveld refinement plot of the neutron diffraction data at 1.5 K. The ticks are given for the nuclear structure peaks (upper), magnetic structure peaks ($Mn^{4+}$ sublattice, middle) and magnetic structure peaks ($Mn^{3+}$ sublattice, lower). Points are the experimental data, line is the Rietveld fit and the lower line is the difference curve.

Figure 3: Lattices parameters of $Nd_{0.5}Ca_{0.5}MnO_3$ as a function of temperature. The charge order transition $T_{CO}$ is indicated by an arrow.

Figure 4: Representation of the CE-type magnetic structure. This structure is characterized by two Mn sublattices forming ferromagnetic zig-zag chains in the a-c plane.

Figure 5: Magnetic moment of the manganese ions as a function of temperature.

Figure 6: Electric resistivity as a function of temperature. The antiferromagnetic transition $T_N$ is indicated by an arrow.

Figure 7: DC susceptibility (10mT) as a function of temperature.
Figure 8: Inverse of the susceptibility at high temperature. The dotted line is a linear fit giving a Curie temperature $\theta_1 = 216K$ and an effective moment $\mu_{eff} = 5.30\mu_B$. 

Figure 9: DC magnetization as a function of magnetic field:

(a) $T = 290K$ (paramagnetic domain)

(b) $T = 211K$ and (c) $T = 183K$ (charge order domain)

(d) $T = 130K$ (antiferromagnetic domain)

Figure 10: Magnetic phase diagram of $Nd_{0.5}Ca_{0.5}MnO_3$. $T_{CO}$ and $T_N$ are determined from neutron diffraction data. The different lines are guides to the eyes to separate the different phases: paramagnetic (P), charge ordered (CO), antiferromagnetic, orbital ordered (AF-O) and ferromagnetic (FM) phases. The dotted line corresponds to the average spin flop field.

Figure 11: Magnetization as a function of temperature for the high field ferromagnetic phase at 20T and 15T.

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Figure 1
Figure 2
Figure 3
Figure 4
Figure 5

Magnetic moment ($\mu_B$) vs. $T$ (K)

- **Mn$^{4+}$**
- **Mn$^{3+}$**
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10

Magnetic Field (T)

Temperature (K)
Figure 11