Magnetic and Electric properties of $La_{1-\delta}MnO_3$

S. de Brion$^1$, F. Ciorcas$^1$, G. Chouteau$^1$, P. Lejay$^2$, P. Radaelli$^3$, C. Chaillout$^4$

$^1$Grenoble High Magnetic Field Laboratory
MPI-FKF and CNRS
BP 166-38042 Grenoble cedex 9, France

$^2$CRTBT
CNRS, BP 166-38042 Grenoble cedex 9, France

$^3$ILL, BP 156-38042 Grenoble cedex 9, France

$^4$Laboratoire de Cristallographie
CNRS, BP 166-38042 Grenoble cedex 9, France

The magnetic phase diagram of $La_{1-\delta}MnO_3$ powdered samples have been studied as a function of $\delta$ in the low doping range. $La_{0.97}MnO_3$ has a canted magnetic structure at low temperature ($\theta \simeq 130^\circ$). Above $T_C = 118K$, it becomes a paramagnet with a huge effective magnetic moment, $\mu_{\text{eff}} = 6.0\mu_B$, reflecting the presence of magnetoelastic polarons which are not affected by the magnetic field (up to 20T) nor the temperature ($1.2T_C < T < 2.5T_C$). When $\delta$ is increased to $\delta = 0.09$, polarons are still present at high temperature, with a smaller size: $\mu_{\text{eff}} = 5.8\mu_B$. The system becomes fully ferromagnetic below 170K but remains insulating down to the lowest temperature.

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I. INTRODUCTION

The manganite compounds $L_{1-x}M_xMnO_3$ where $L = La, Nd, Pr, ...$ and $M = Sr, Ba, Ca, ...$, exhibit a variety of unexpected properties such as colossal magnetoresistance \[1\], field induced structural transition \[3\], charge ordered state \[4\], etc. These properties depend crucially on the doping level as well as the nature of the doping element \[6\]. They are closely related to the mixed valence Mn(III)-Mn(IV).

These compounds have been studied for a long time \[3\], \[5\]. $LaMnO_3$ contains $Mn^{3+}$ ions ($S = 2$). It is antiferromagnetic ($T_C \approx 140K$) and insulating. It becomes ferromagnetic and metallic upon hole doping (introduction of $Mn^{4+}$ ions) with the maximum of $T_C$ reached when the $Mn^{4+}$ concentration is around $x \approx 0.35$. C. Zener \[7\] proposed a mechanism of double exchange between the itinerant $e_g$ electrons and the localized $t_{2g}$ electrons forming $S = 3/2$ ions ($Mn^{4+}$). In this process, the electrons tend to move from one ionic site to another with the same spin orientation; therefore electron delocalization favors ferromagnetism. P.W. Anderson and H. Hasegawa \[8\], P.G. de Gennes \[9\], K. Kubo and N. Ohata \[10\] further developed this theory. Recent calculations \[11\] have shown that double exchange alone cannot account for the observed colossal magnetoresistance. Magneto-elastic effects are very important in these compounds \[2\], \[12\]. Several theoretical attempts have been made to incorporate electron-phonon coupling \[13\], \[14\] leading to the idea of lattice polarons above the ferromagnetic transition. However, this lattice polaron picture remains controversial: C.M. Varma \[15\] proposed rather the idea of spin polarons driven by thermal fluctuations and electron-electron correlations.

Experimentally, there are some evidences for the existence of polarons \[12\], \[16\], \[17\], \[18\]. But their nature, their extension as a function of temperature and their dependence on doping is not clear. In this paper, we will focus on the low doping regime, close to the parent compound $LaMnO_3$, to look at the progressive establishment of ferromagnetism and metallicity and to study the polaronic effect.

For small doping concentration, several magnetic structures have been observed at low temperature. In $La_{1-x}Sr_xMnO_3$ \[2\], a canted magnetic structure is present for $x \lesssim 0.08$, a ferromagnetic insulator for $0.08 \lesssim x \lesssim 0.16$ and a ferromagnetic metal above. In $La_{1-x}Ca_xMnO_3$ \[2\], the compound has been reported as a ferromagnetic insulator for $x \lesssim 0.15$ and a ferromagnetic metal above. However, a different magnetic structure has been observed by H. Henning et al \[13\]: they found that, for $x = 0.05$ and $x = 0.08$, the compound is antiferromagnetic. For the parent compound $LaMnO_3$ \[2\], a variety of magnetic and crystallographic structures have been observed due to off-stoichiometry on the Lanthanum as well as the Manganese sites: antiferromagnetic, canted, spin glass, ferromagnetic (($T_C \simeq 150K$) and insulating. It becomes ferromagnetic and metallic upon hole doping \[1\]. We will present evidences for polarons in both samples at high temperature (above the magnetic ordering temperature) and we will discuss their role in the magnetic and electric properties of the compound as a function of doping. Comparison with other manganites with different doping element will be presented.

II. SAMPLES PREPARATION AND CHARACTERIZATION

Polycrystalline samples were prepared through a conventional solid state reaction. The starting materials were $La_2O_3$ (calcined 4N pure) and dried $MnO_2$. Stoichiometric amounts of these powders were mixed and heated at 900°C for 12 hours in alumina crucibles. After regrinding, the black powders were pellet pressed and sintered in an oxygen gas flow during 24 hours at 950°C. Additional treatments at 950°C under flowing oxygen or purified argon have been carried leading to different off-stoichiometry. In each case, the samples were cooled down at a rate of 100°C per hour. An X-ray diffraction pattern was performed on each sample and analyzed using a Rietveld analysis. The results for two typical samples LMO94R and LMO104RO3 are presented in table I. LMO94R is orthorhombic whereas LMO104RO3 is rhombohedral. Presence of $Mn_3O_4$ was detected in LMO94R.

Neutron diffraction data were collected on the high resolution diffractometer D2B at ILL, Grenoble, to determine whether these samples had a different cationic or oxygen stoichiometry. The structure has been refined by the Rietveld method, using the Pnma space group for sample LMO94R and R-3C for sample LMO104RO3. From the refined values of the occupancy factors, it has been seen that these samples present La deficiency: $La_{0.97}MnO_3$ and $La_{0.93}MnO_3$ respectively (see table I). This means that the exact formula is $La_{1-\delta}MnO_3$. The samples then contain $Mn^{4+}$ ions with the concentration $3\delta$. 

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III. MAGNETIC PROPERTIES

Off stoichiometry in $LaMnO_3$ has been widely reported [2], and is known to modify the crystallographic and magnetic structure. Indeed, $La_{0.97}MnO_3$ and $La_{0.93}MnO_3$ have a very different magnetic behavior. To characterize them, AC susceptibility and low field DC magnetization measurements were used in the temperature range 4K-350K. The field dependence of the magnetization was recorded with an extraction method in a field up to 20 T at different temperatures, in the range 4K-300K. The electrical resistivity was also measured in the same field and temperature range using a DC technique for resistance up to $10^5$ Ohm. The powdered samples were then pellet pressed and silver paste was used for electric contacts.

$La_{0.93}MnO_3$ is ferromagnetic below $T_C = 170K$ (figure 1). Here, the ordering temperature is taken at the inflection point on the susceptibility curve. At 4K, the magnetization saturates in a field of 1 Tesla and remains constant up to 20 Tesla with a value $M_s = 3.2 \mu_B$. This value should be compared to the expected one. For both $Mn^{3+}$ and $Mn^{4+}$, the orbital momentum is quenched so that the magnetic moment reduces to the spin contribution $gS\mu_B$ where S is the spin of the ion (3/2 for $Mn^{4+}$ and 2 for $Mn^{3+}$) and $g$ is the gyromagnetic factor ($g = 2$ for both). For 1-x $Mn^{3+}$ ions and x $Mn^{4+}$ ions, it becomes $(4 - x)\mu_B$. Taking the value of x from the neutron diffraction results, we get $3.79 \mu_B$, a value higher than observed. This discrepancy may have two different origins. Either it arises from the presence of disorder in the sample, although $M_s$ is not affected by a magnetic field up to 20 Tesla. No spin glass behavior has been detected (the ordering temperature does not depend on the measurement frequency; the magnetization at low temperature does not depend on time). More probably, this overestimation reveals that the simple calculation for the saturation moment is affected by collective effects and/or spin orbit coupling.

Above the ordering temperature, the system behaves quite differently from what is expected: the magnetic susceptibility does not follow a Curie-Weiss law. To have a better understanding of the paramagnetic regime, we have analyzed the magnetization curves as a function of field within a mean field approximation model. The internal field $H_i$ seen by the magnetic moments has three contributions: the applied field $H_a$, the demagnetization field $H_d$ and the molecular field $H_m$ due to the magnetic coupling. In a mean field approximation, this molecular field can be described by a single parameter $\lambda$ such that $H_m = \lambda M$ where $M$ is the magnetization. The demagnetization field is given by $H_d = nM$ where $n$ is the demagnetization factor. Our powdered samples may be considered as spheres for which $n = 1/3$. This demagnetization field is quite small compared to the applied field ($\mu_0 H_d \approx 0.3T$ when the magnetization is at its maximum value $M = 3.2 \mu_B$ whereas $\mu_0 H_a$ varies up to 20T). We have plotted, in the insert of figure 2, the magnetization as a function of $H_i/T$. All the magnetization curves collapse on a single curve in the temperature range 100K-300K if the mean field parameter is taken as temperature dependent (see figure 2). This is in agreement with the susceptibility data which do not follow the mean field Curie-Weiss law. The curve $M (H/T)$ can be fitted with a single Brillouin function from which we deduce an effective magnetic moment $\mu_{eff}$. We get $\mu_{eff} = 5.8 \mu_B$. In a mean field approximation, for one type of magnetic ions, $\mu_{eff}$ is given by $\mu_{eff} = g^2 S(S + 1)\mu_B^2$ where $x$ is the fraction of magnetic ions per formula unit, $g$ is their gyromagnetic factor and $S$ their spin. $La_{0.93}MnO_3$ contains $Mn^{3+}$ and $Mn^{4+}$ ions. We can treat them as one type of ions with an average spin $S = 2(1 - x) + \frac{3}{2}x$ with $x = 0.21$, which lead to $\mu_{eff} = 4.68 \mu_B$. Or we can treat them as separated magnetic systems with the same ordering temperature. then $\mu_{eff}^2 = \mu_{eff1}^2 + \mu_{eff2}^2$ and $\mu_{eff} = 4.44 \mu_B$. In both cases, the observed value is much bigger. It is the signature of clusters of $Mn^{4+}$ and $Mn^{3+}$.

$La_{0.97}MnO_3$ behaves quite differently. A peak in the AC susceptibility is observed at 118K (figure 3, upper part). The additional peak at 49K is related to $MnO_4$. The DC susceptibility shows hysteresis below 118K revealing the presence of ferromagnetic domains: it has a more ferromagnetic like behavior (figure 3, lower part). The magnetization curves as a function of field at low temperature present a spontaneous magnetization followed by a high field susceptibility (figure 4). These features are characteristics of a canted magnetic structure. This was confirmed by neutron diffraction data. At 2.5K, the ferromagnetic moment is 1.48$\mu_B$ and the antiferromagnetic moment 2.93$\mu_B$, so that the canting angle is 130°. The measured high field susceptibility, $\chi \approx 8.75 \times 10^{-2} \mu_B/T \approx 1.74 \times 10^{-2} S.I.$, is temperature independent from 4K up to 100K at least. We have also observed some hysteresis up to 20T. This hysteresis exists in a limited temperature range: $T < 80K$ (figure 5).

Above the ordering temperature, we have analyzed the magnetization curves in terms of a mean field theory, similarly to $La_{0.93}MnO_3$. The molecular field parameter is constant from 300K until 150K (figure 2), which suggests that a mean field approach is correct. The effective moment deduced from a Brillouin fit is $\mu_{eff} = 6.0 \mu_B$. For this concentration also, clusters are present. The calculated mean field ordering temperature is $T_P = 114K$, a value very close to the observed transition temperature ($T_C = 118K$).

IV. ELECTRIC TRANSPORT
Both samples remain insulating (figure 5) with activation energies of the order of 0.16 eV. No anomalies or change of slope have been detected at the ordering temperature. Application of a magnetic field reduces the magnitude of the electric resistivity, $\rho$, is plotted as a function of the magnetization $M$, quite different behavior are observed for each sample. The canted sample, $La_{0.97}MnO_3$, presents a universal law for $\rho(M)$ down to 120 K: $\rho(M) / \rho(0) = 1.25 (M/M_s)^2$ (see figure 6). Measurements were restricted to $T \geq 120K$ because of the high resistivity. At 120K, around the ordering temperature, an additional process contributes to the electric transport at low magnetization. It is probably related to magnetic domains.

The ferromagnetic sample behaves very differently. The square dependence of the magnetoresistance on the magnetization is no longer observed. Actually, no universal dependence can be deduced. Granular effects are probably too important.

V. DISCUSSION

The fundamental electronic structure of these mixed valence oxides have been reviewed by J.B. Goodenough [22]. $LaMnO_3$ involves $Mn^{3+}$ ions in the $t^2_g e^1_p$ ($S = 2$) configuration. These are Jahn-Teller ions. $LaMnO_3$ is well described by a localized electron model. In the Mn-O-Mn plane, the half filled $e_g$ orbital couples to an empty $e_g$ orbital, leading to a ferromagnetic coupling. In the perpendicular direction, coupling between half filled $t_{2g}$ orbitals leads to antiferromagnetism. $LaMnO_3$ has therefore a layered antiferromagnetic structure.

When doping by substituting the trivalent La ion by divalent ions such as Ba, Ca, Sr, ... (or adding oxygen), $Mn^{4+}$ ions are introduced. They are in the $t^2_g e^2_p$ ($S = 3/2$) configuration. Above a critical concentration of the order of 0.1, the $e_g$ electrons are delocalized. Due to their intrinsic spin and strong correlation with the localized $t_{2g}$ electrons, they hop from a $Mn^{3+}$ site to a $Mn^{4+}$ site having the same spin orientation. This so-called double exchange gives rise to a ferromagnetic metallic state. The transfer energy between two ionic sites having spins making an angle $\theta_{ij}$ is expressed by [12]:

$$t_{ij} = b_{ij} \cos(\theta_{ij}/2).$$

This introduces a canting of the spin; $\theta$ increases with $Mn^{4+}$ content until complete ferromagnetism is reached [9], around $x \approx 0.3$. The canted state is characterized by a spontaneous magnetization $M_s$, which is related to the canting angle $\theta$:

$$M_s = I \cos(\theta/2),$$

$$\cos(\theta/2) = bx/4|J|S^2.$$  

and by a high field susceptibility which is roughly equal to the perpendicular susceptibility of the antiferromagnetic parent compound $LaMnO_3$:

$$\chi_\perp = (I/4)(\gamma_0 S^2 N).$$

Here $I/2$ is the sublattice magnetization, $x$ the $Mn^{4+}$ concentration, $J$ the antiferromagnetic coupling, $b$ the double exchange coupling, $N$ the number of magnetic ions per unit cell ($N = 1$), $S$ their spin and $\gamma_0$ the number of their neighbors in the adjacent layers ($\gamma_0 = 2$).

The above features have been derived by P.G. de Gennes assuming a pure canted spin arrangement, such that the spins form two sublattices separated by an angle $\theta$. However, J. Inoue et al [23] have pointed out that the pure canted state should be more stable close to $x = 1$ and a spiral state close to $x = 0$.

In both cases, the spin in one set of Mn-O plane is rotated by an angle from the adjacent Mn-O plane. The distinction between these two arrangements is the following: in the pure canted state, there are two sublattices making an angle $\theta$ with each other. The magnetic periodicity is therefore twice the lattice periodicity in the direction perpendicular to the Mn-O planes. In the spiral state, the successive planes make an angle $\theta$, $2\theta$, $3\theta$, ... with respect to a reference plane. The periodicity can be large, $\theta/2\pi$ times the lattice periodicity and incommensurability effects may occur. The model by P.G. de Gennes should not be substantially affected whether the spin arrangement is of the pure canted or spiral type.

E.O. Wollan et al [3] have reported evidences for pure canted spins at low concentration. Their data agree with equation (2). Our experimental results for $La_{0.97}MnO_3$ agree quite well also with such a picture: the magnetization curve present a spontaneous magnetization followed by a temperature independent susceptibility. The spontaneous magnetization is in agreement with the value of the canting angle deduced from neutron diffraction data. From the high field susceptibility, $\chi \approx 1.74 \times 10^{-2} S.I.$, we can estimate the antiferromagnetic coupling, using the average value for $S$ ($S = 1.96$): $J \approx -4.0K \approx -0.36meV$. This value should be compared to the one deduced from spin wave measurements: in pure $LaMnO_3$, $J \approx -5.8meV$ [24]; in $La_{0.95}Ca_{0.05}MnO_3$, it is reduced to $J \approx -0.38meV$ [18], and in $La_{0.95}Ca_{0.05}MnO_3$, to $J \approx -0.28meV$; in $La_{0.95}Sr_{0.05}MnO_3$, it is $J \approx -0.20meV$ [20]. Our results are in good agreement with those of $La_{1-x}Ca_xMnO_3$. The antiferromagnetic interaction is reduced in the similar way when doping is introduced through Lanthanum vacancies or through Calcium doping. This is not very surprising considering the great mismatch between the size of Lanthanum ions ($r = 0.122nm$) and the one of Calcium ions ($r = 0.106nm$).
On the contrary, doping through Strontium ions is different since its ionic radius is bigger \((r = 0.126 \text{nm})\). The overlap of the oxygen and manganese orbitals is modified in a different way.

Using equation (2), we can extract the double exchange coupling: \(b \approx 290 K\). In term of energy, the double exchange coupling contributes to an amount of \(E_{d1} = -4bx \approx -104K\) and \(E_{d2} = -2\frac{k^2x^2}{4|J|S^2} \approx -22K\); the first term refers to the double exchange energy within one Manganese plane and the second term to the double exchange energy from one plane to the adjacent planes. The antiferromagnetic contribution from one plane to the adjacent ones is \(E_{AF} = 2|J|S^2 \cos \theta_0 \approx -20K\). The ferromagnetic contribution arising from the indirect exchange coupling between manganese ions in the same plane is given by \(E_F = -4J'S^2\) where \(J'\) is the ferromagnetic indirect coupling. In \(La_{0.97}Ca_{0.03}MnO_3\), \(J' \approx 12K\) which leads to \(E_F \approx -184K\). In term of energy, the double exchange contribution has the same order of magnitude as the antiferromagnetic contribution \((-22K\) and \(-20K\) respectively). It is not strong enough to establish complete ferromagnetism. The slope of the function \(\cos \theta_0\) as a function of \(x\) is similar to what is observed in \(La_{1-x}Ca_xMnO_3\) and this system, in term of exchange interactions at least.

At low temperature, a high field hysteresis is present below 80K (see figure 4). Repeated magnetization curves show a random behavior between two extrema curves. We propose that this hysteresis finds its origin in the different canted structures that are possible with a fixed canting angle i.e. spiral or pure canted or mixture. It is not a field induced phase transition but it reflects rather the presence of different metastable configurations for the spins. However we did not detect any time dependent effects on the magnetization, at least on a time scale of a couple of hours. The disappearance of this hysteresis above 80 K can be explained by thermal activation effects. It can also be explained by the occurrence of a charge ordered phase present only at low temperature.

P.G. de Gennes has calculated the characteristic ordering temperatures \(T_C\) and \(T_P\) where \(T_C\) is the ordering temperature and \(T_P\) the paramagnetic Curie point defined through the asymptotic form of the susceptibility \(\chi = C/ (T - T_C)\). He found that they should coincide: \(k_B T_C = k_B T_P = \frac{4}{9} \left( \frac{2 |J| + 4 J'}{S^2} - \frac{3}{2} \xi_0 \right)\), where \(J'\) takes into account the modification arising from the Zener carrier \((J'\) increases with \(x\) as has been observed in \(|12|\). Taking the values determined above for \(J, J'\) and \(b\), we get: \(T_C = T_P \approx 130K\). Experimentally, we do observe \(T_C \approx T_P\) with a slightly smaller value (114K). The treatment by P.G. de Gennes seems quite appropriate.

At higher temperature, the paramagnetic regime is however not conventional: it is described by an effective magnetic moment which is much bigger than expected. This is the signature of magnetic clusters. Many combinations of \(Mn^{3+}, Mn^{4+}\) can give rise to \(\mu_{eff} = 6.0 \mu_B\) so that it is difficult to extract the exact size of these clusters. The magnetic field does not affect their size nor their number, since we observe a single Brillouin function as a function of \(H\) susceptibility from a Curie law is usually observed above \(T\). It depends on the doping concentration as well as the nature of the doping element. For instance, deviation of the exchange coupling contributes to an amount of \(E = 2 |J| S^2 \cos \theta_0 \approx -20K\). The ferromagnetic contribution arising from the indirect exchange coupling between manganese ions in the same plane is given by \(E_F = -4J'S^2\) where \(J'\) is the ferromagnetic indirect coupling. In \(La_{0.97}Ca_{0.03}MnO_3\), \(J' \approx 12K\) which leads to \(E_F \approx -184K\). In term of energy, the double exchange contribution has the same order of magnitude as the antiferromagnetic contribution \((-22K\) and \(-20K\) respectively). It is not strong enough to establish complete ferromagnetism. The slope of the function \(\cos \theta_0\) as a function of \(x\) is similar to what is observed in \(La_{1-x}Ca_xMnO_3\) and this system, in term of exchange interactions at least.

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What is the origin of these clusters? In these materials, presence of polarons has been detected \(|12|\). It depends on the doping concentration as well as the nature of the doping element. For instance, deviation of the susceptibility from a Curie law is usually observed above \(T_C\). In \(La_{0.66}Ca_{0.33}MnO_3\), it occurs below \(1.8T_C\) and is accompanied by the formation of magneto-elastic polarons. Their coherence length increases when the temperature is lowered and eventually diverges at \(T_C\). It also increases with magnetic field with a typical value at zero field of \(1.2nm\). Above \(1.8T_C\), a Curie-Weiss law is recovered with an effective moment corresponding to isolated manganese ions. \(La_{0.97}MnO_3\) is an insulator in the whole temperature range. The polaronic effect is different: magnetic clusters are present at much higher temperature (until \(2.5T_C\) at least) with a size remaining constant in the whole temperature and field range studied. Deviation from a Curie law occurs only when \(T < 1.2T_C\), the magnetic polaron is more strongly established in \(La_{0.97}MnO_3\) than in \(La_{0.66}Ca_{0.33}MnO_3\). The magneto-elastic interaction which is responsible for its formation is much stronger. This polaronic effect depends on the doping concentration. In \(La_{1-x}Ca_xMnO_3\), S.J.Billinge et al. have observed lattice polarons above the ferromagnetic transition for \(x = 0.25\) and \(x = 0.21\), but none for \(x = 0.12\) which does not present an insulating to metallic transition like the others at the ferromagnetic transition. This is in contrast to our results where we observe polarons in \(La_{0.97}MnO_3\) which is even less doped; but this is consistent with the idea that the polarons are ‘stronger’ in \(La_{1-x}MnO_3\) than in \(La_{1-x}Ca_xMnO_3\).

Several theoretical treatments of the polaronic effects have been proposed. A.J.Millis et al. conclude that, for intermediate doping, strong electron-phonon coupling localizes the conduction electrons as polarons for \(T > T_C\) and that the effect is turned off at \(T_C\). H.Röder et al. arrive to the same conclusion. They were able to reproduce the doping dependence of the ferromagnetic transition \(T_C\) and found that, for \(T > T_C\), in the dilute limit, small magnetopolarons are formed and comprise a localized charge surrounded by a spin cloud. They have shown that the size of the polaron grows as the ordering temperature is approached from above, in agreement with the experimental results on \(La_{0.66}Ca_{0.33}MnO_3\). This lattice polaron picture remains controversial: C.M. Varma proposed rather the idea of spin polarons due to random hoping driven by thermal fluctuations and electron-electron correlation. He found also that the magnetic susceptibility should be enhanced above \(T_C\) with a temperature dependent effective moment, in a first approximation at least.
All these theoretical works are only concerned with the ferromagnetic metallic phase and do not seem appropriate for $La_{0.97}MnO_3$. Indeed, in this sample, the size of the polarons is not temperature dependent in the paramagnetic regime, which is major difference compare to the ferromagnetic metallic phases. But we may have observe precursor effects.

Does this clustering persist in the ordered phase? At low temperature, the magnetization measurements agree quite well with de Gennes’s theory of canted spins. However this cannot rule out the existence of clusters; as was pointed out by P.G. de Gennes, the same magnetic behavior is expected both for long range order or bound states. In a sample with the same doping level, M. Hemion et al. have observed, at low temperature, magnetic excitations that they have interpreted as magnetic polarons. They disappear above the ordering temperature. It is quite different in our sample where the magnetic polarons exist in the paramagnetic phase.

This different behavior should be accounted for because of the different nature of doping in both samples: for $La_{0.97}MnO_3$, vacancies on the lanthanum is the doping factor whereas in $La_{1-x}Ca_xMnO_3$, doping is introduced by replacing lanthanum ions by the smaller calcium ions. The lattice mismatch is greater in $La_{1-x}Ca_2MnO_3$ than in $La_{1-x}CaMnO_3$. The magnetic order is affected: $La_{0.97}MnO_3$ has a canted structure with $\theta \approx 130^\circ$, while $La_{0.97}Ca_{0.08}MnO_3$ is antiferromagnetic ($\theta \simeq 170^\circ$). The polaronic effect is also affected. $La_{0.95}Ca_{0.05}MnO_3$ and $La_{0.95}Sr_{0.05}MnO_3$, have the same doping level (5% of $Mn^{4+}$) and the same antiferromagnetic magnetic structure. Magnetic excitations have been detected at low temperature for the former and none for the later. These results confirm that the strength of the polarons depends crucially on the nature of the doping element due to the modification of the electron-phonon coupling as well as the magnetic interactions.

If polarons are present, the resistivity is expected to follow the variable range hoping law. We only observe an activated behavior as a function of temperature. This is consistent with the fact that the polarons remains constant in size. We observe a simple law for $\rho (M)$: $\rho (M) / \rho (0) = C (M/M_0)^2$ with $C \simeq 1.25$ (see figure 6). Such a law has been predicted by N.Furukawa. His calculation is based on spin fluctuations. He shows that the constant $C$ depends both on the doping level and the Hund coupling between the $e_g$ electrons and the localized $S = 3/2$ spins. Numerical values for $C$ are given for higher doping concentration than $La_{0.97}MnO_3$ but we can extrapolate to lower concentration: the tendency is to get a higher value of $C$ when the doping is decreased, at least in the strong Kondo coupling limit, as it is the case in these compounds. In $La_{0.97}MnO_3$, we get a value of $C$ plausible only in the weak coupling limit. This is in contrast to what is observed in $La_{1-x}Sr_xMnO_3$ where the value of $C$ is about 4 for $0.15 \leq x \leq 0.2$, and decreases to 2 for $x = 0.3$ and about 1 for $x = 0.4$.

So far, we have discussed the properties of $La_{0.97}MnO_3$. How are they affected when more vacancies are introduced? First of all, the system becomes ferromagnetic (with complete saturation at 4K), as expected from double exchange theory. It is remarkable to notice, though, that $La_{0.93}MnO_3$ never achieves a metallic conductivity. Indeed no anomaly in the resistivity has been observed down to 50K even in high magnetic field. A similar ferromagnetic insulating phase has been observed in $La_{0.90}Sr_{0.10}MnO_3$ and in $LaMnO_3$. At first sight, this is in contradiction with the idea of double exchange where ferromagnetism is induced by electron hoping and therefore requires an insulator to metal transition when long range ferromagnetic order is established. The existence of a ferromagnetic insulating phase, as in $La_{0.93}MnO_3$, is a clear evidence that not all the Zener electrons responsible for ferromagnetism take part in the conduction process. Electron localization occurs. This is also observe at higher $Mn^{4+}$ content: in $La_{0.7-x}Y_xCa_{0.3}MnO_3$ thin films, with a constant doping level (30% of $Mn^{4+}$), the insulator to metal transition is shifted to lower temperature as a function of yttrium doping and, at the same time, the level of resistivity in the ferromagnetic phase is increased by several order of magnitude.

This localization has been explained by R. Allub et al. They have looked at the effect of localized states introduced by disorder. Their model was successful to account for the change in resistivity in $La_{1-x}Sr_xMnO_3$ where the system is ferromagnetic and insulating for $x < 0.125$. In $La_{1-x}MnO_3$, the insulating state persists to much higher concentration (for $La_{0.93}MnO_3$, $x = 0.21$). Another origin for this insulating behavior may be found in the presence of polarons persistent in the ferromagnetic phase. It has been shown that, in the metallic ferromagnet, the polarons disappears below $T_C$. In $La_{0.93}MnO_3$, similarly to $La_{0.97}MnO_3$, the polaronic effect is much stronger and may remain effective at low temperature. It will localize the electrons. However, the ferromagnetic correlation length will have to be greater than the polaron size to get a full ferromagnetic phase. More theoretical developments are required.

Experimentally, in the paramagnetic regime, we observe a smaller effective moment in $La_{0.93}MnO_3$ than in $La_{0.97}MnO_3$ from 6.0 to 5.8 $\mu_B$. This suggests that the polaron size has decreased. Similar results have been observed by J.Töpfer et al. in $La_{1-x}Mn_{1-x}O_3$. Indeed, we would expect, for even higher vacancy content, to reduce further the size of the polarons to rich a single ion behavior with, at the same time, an enlargement of the critical regime and occurrence of an insulator to metal transition with huge magnetoresistance. However, in this $La_{1-x}MnO_3$ series, the occurrence of a ferromagnetic metallic like phase is reduced as a function of the $Mn^{4+}$ content compare to $La_{1-x}Sr_xMnO_3$ or $La_{1-x}Ca_xMnO_3$. The metallic phase may even not exist, as it is the case for $Pr_{1-x}Ca_xMnO_3$. 6
VI. CONCLUSIONS

We have studied the magnetic and electric properties of $La_{1-\delta}MnO_3$ for two values of $\delta$: $\delta = 0.03$ and $\delta = 0.07$ corresponding to 9% and 21% of Mn$^{4+}$ respectively. Their properties change dramatically. $La_{0.97}MnO_3$ has a canted magnetic structure at low temperature ($\theta \simeq 130^\circ$ and $T_C = 118K$). Its magnetic behavior fits quite well with de Gennes theory of canted spins. We have extracted the values of the double exchange interaction ($b \approx 290K$) and the antiferromagnetic indirect exchange ($J \approx -4.0K$). In the paramagnetic regime, magneto-elastic polarons are present with an effective moment of $\mu_{eff} = 6.0 \mu_B$. Their size is not affected by temperature for $1.2T_C < T < 2.5T_C$, nor by magnetic field ($B < 20T$) contrary to what is observed in the metallic ferromagnet $La_{0.66}Ca_{0.33}MnO_3$. For higher vacancy content, $\delta = 0.07$, polarons are still present but smaller in size; their effective moment is $\mu_{eff} = 5.8 \mu_B$. The system becomes fully ferromagnetic thanks to double exchange, but the compound remains insulating, even in the ferromagnetic phase.

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VII. FIGURES

Figure 1: Temperature dependence of the magnetic susceptibility in $La_{0.93}MnO_3$.
upper part: AC susceptibility
lower part: DC susceptibility in a field of 5mT (zero field cooling and field cooling curves). Insert: Magnetization as a function of field at 4K.

Figure 2: Mean field parameter $\lambda$ as a function of temperature for $La_{0.97}MnO_3$ and $La_{0.93}MnO_3$. Insert: Magnetization as a function of $g\mu_BH_i/kT$ for $La_{0.93}MnO_3$.

Figure 3: Temperature dependence of the magnetic susceptibility in $La_{0.97}MnO_3$.
upper part: AC susceptibility
lower part: DC susceptibility in a field of 5mT (zero field cooling and field cooling curves).

Figure 4: Field dependence of the magnetization in $La_{0.97}MnO_3$. Insert: Hysteresis field $H_h$ as a function of temperature.

Figure 5: Temperature dependence of the electrical resistivity in $La_{0.93}MnO_3$ and $La_{0.97}MnO_3$ without and with a 20 Tesla magnetic field.

Figure 6: Resistivity as a function of magnetization for $La_{0.97}MnO_3$. 

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| sample   | formula      | $Mn^{4+}$ content | space group | cell parameters   |
|----------|--------------|-------------------|-------------|------------------|
| LMO94R   | $La_{0.97}MnO_3$ | 9%                | Pnma        | $a = 0.56290nm$  |
|          |              |                   |             | $b = 0.77248nm$  |
|          |              |                   |             | $c = 0.55410nm$  |
| LMO104   | $La_{0.93}MnO_3$ | 21%               | R-3C        | $a = 0.55245nm$  |
|          |              |                   |             | $c = 1.33433nm$  |

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Magnetization ($\mu_B / Mn$) vs. Magnetic Field (T) at 30 K and 100 K.

Inset: $H_h$ vs. T (K) for T = 100 K.

Magnetization ($\mu_B / Mn$) increases with increasing Magnetic Field (T) at both 30 K and 100 K.
La$_{0.97}$MnO$_3$
La$_{0.93}$MnO$_3$

Temperature (K)

$M / H$ (a.u.)

$X_{ac}$ (a.u.)