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

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The magnetic phase diagram of $La_{1-\delta}MnO_3$ powdered samples has been studied as a function of δ in the low doping range ($\delta<0.1$). $La_{0.97}MnO_3$ has a canted magnetic structure at low temperature ($\theta\simeq 130°$). Above $T_C=118$ K, it becomes a paramagnet with a huge effective magnetic moment $\mu_{\mathrm{eff}}=6.0\mu_B$, reflecting the presence of magnetoelastic polarons which are not affected by the magnetic field (up to 20 T) or the temperature $1.2T_C<T<2.5T_C$. When δ is increased to $\delta=0.09$, the system becomes fully ferromagnetic below 170 K but remains insulating down to the lowest temperature. [S0163-1829(99)16101-0]

I. INTRODUCTION

The manganite compounds $L_{1-x}M_x MnO_3$, where $L=La,Nd,Pr,\ldots$, and $M=Sr,Ba,Ca,\ldots$, exhibit a variety of unexpected properties such as colossal magnetoresistance,[1] field induced structural transition,[2] charge ordered state,[3] etc. These properties depend crucially on the doping level as well as the nature of the doping element.[4] They are closely related to the mixed valence Mn(III)-Mn(IV).

These compounds have been studied for a long time.[5,6] $LaMnO_3$ contains Mn^{3+} ions ($S=2$). It is antiferromagnetic ($T_N\simeq 140$ K) 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 $x\simeq 0.35$. 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. Anderson and Hasegawa,[8] de Gennes,[9] 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. Magnetoelastic 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: Varma[15] proposed rather the idea of spin polarons driven by thermal fluctuations and electron-electron correlations.

Experimentally, there are some evidence for the existence of polarons.[12,16–18] 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 $La_{1-x}Sr_xMnO_3$,[19] 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 $La_{1-x}Ca_xMnO_3$,[20] 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 Hennion *et al.*:[18] they found that for $x=0.05$ and $x=0.08$ the compound is, on the average, antiferromagnetic with a small ferromagnetic component; but this phase is not homogeneous (presence of magnetic droplets). For the parent compound $LaMnO_3$,[5,21] 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 insulators, or even ferromagnetic metals. These examples are an illustration that the magnetic phase diagram depends on the doping element as well as off-stoichiometry effects.

The samples studied here are doped in Mn^{4+} through off stoichiometry in lanthanum. Their stoichiometry and crystallographic structure have been determined by neutron diffraction. We have investigated the magnetic and electric properties of two samples with different stoichiometries: 9 and 21% of Mn^{4+}. We will show how the magnetic phase diagram evolves as doping is increased (from a canted magnetic structure to a ferromagnet), how it influences their electric transport (both samples are insulators down to low temperature), and their magnetoresistivity. We will present evidence for polarons in both samples at high temperature (above the magnetic ordering temperature) and we will discuss their

TABLE I. Stoichiometry and crystallographic parameters of two typical samples.

Sample	Formula	Mn^{4+} content	Space group	Cell parameters
LMO94R	$La_{0.97}MnO_3$	9%	*Pnma*	$a=0.56290$ nm $b=0.77248$ nm $c=0.55410$ nm
LMO104	$La_{0.93}MnO_3$	21%	R-3C	$a=0.55245$ nm $c=1.33433$ nm

role in the magnetic and electric properties of the compound as a function of doping. Comparison with other manganites with different doping elements will be presented.

II. SAMPLE 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 h in alumina crucibles. After regrinding, the black powders were pellet pressed and sintered in an oxygen gas flow for 24 h 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 h. 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 be 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 3δ.

III. MAGNETIC PROPERTIES

Off stoichiometry in $LaMnO_3$ has been widely reported,[21] 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 4–350 K. 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 4–300 K. The electrical resistivity was also measured in the same field and temperature range using a dc technique for resistance up to $10^7\Omega$. The powdered samples were then pellet pressed and silver paste was used for electric contacts.

$La_{0.93}MnO_3$ is ferromagnetic below $T_C=170$ K (Fig. 1). Here, the ordering temperature is taken at the inflection point on the susceptibility curve. At 4 K, the magnetization saturates in a field of 1 T and remains constant up to 20 T 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 T. 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,

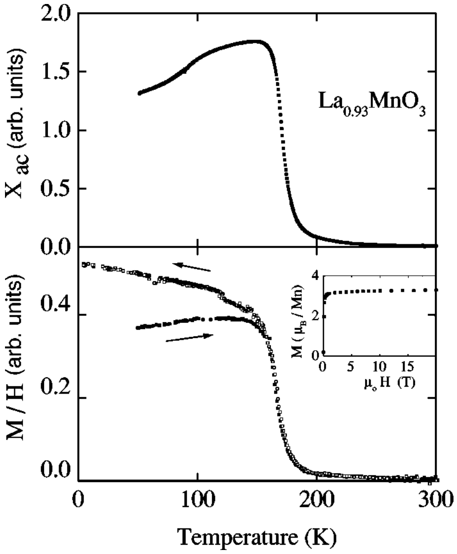

FIG. 1. Temperature dependence of the magnetic susceptibility in $La_{0.93}MnO_3$. Upper part: ac susceptibility; lower part: dc susceptibility in a field of 5 mT (zero field cooling and field cooling curves). Inset: Magnetization as a function of field at 4 K.

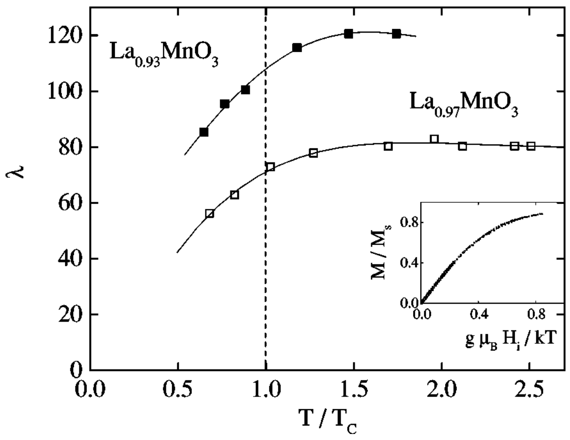

FIG. 2. Mean field parameter λ as a function of temperature for $La_{0.97}MnO_3$ and $La_{0.93}MnO_3$. Inset: Magnetization as a function of $g\mu_B H_i/kT$ for $La_{0.93}MnO_3$.

this molecular field can be described by a single parameter λ 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 ($\mu_0 H_d \simeq 0.3$ T when the magnetization is at its maximum value $M = 3.2\mu_B$ whereas $\mu_0 H_a$ varies up to 20 T). We have plotted in the inset of Fig. 2, the magnetization as a function of H_i/T. All the magnetization curves collapse on a single curve in the temperature range 100–300 K if the mean field parameter is taken as temperature dependent (see Fig. 2). This is in agreement with the susceptibility data which do not follow the mean field Curie-Weiss law. The curve $M(H_i/T)$ can be fitted with a single Brillouin function from which we deduce an effective magnetic moment μ_{eff}. We get $\mu_{\mathrm{eff}} = 5.8\mu_B$. In a mean field approximation, for one type of magnetic ions, μ_{eff} is given by $\mu_{\mathrm{eff}}^2 = xg^2S(S+1)\mu_B^2$, 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 $\mu_{\mathrm{eff}} = 4.68\mu_B$. Or we can treat them as separated magnetic systems with the same ordering temperature. Then $\mu_{\mathrm{eff}}^2 = \mu_{\mathrm{eff1}}^2 + \mu_{\mathrm{eff2}}^2$ and $\mu_{\mathrm{eff}} = 4.70\mu_B$. 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 118 K (Fig. 3, upper part). The additional peak at 43 K is related to Mn_3O_4. The dc susceptibility shows hysteresis below 118 K revealing the presence of ferromagnetic domains: it has a more ferromagneticlike behavior (Fig. 3, lower part). The magnetization curves as a function of field at low temperature present a spontaneous magnetization followed by a high field susceptibility (Fig. 4). These features are characteristics of a canted magnetic structure. This was confirmed by neutron diffraction data. At 2.5 K, 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, $\chi \simeq 8.75 \times 10^{-2} \mu_B/T \simeq 1.74 \times 10^{-2}$ SI, is temperature independent from 4 K up to 100 K at least. We have also observed some hysteresis up to 20 T. This hysteresis exists in a limited temperature range $T < 80$ K (Fig. 5).

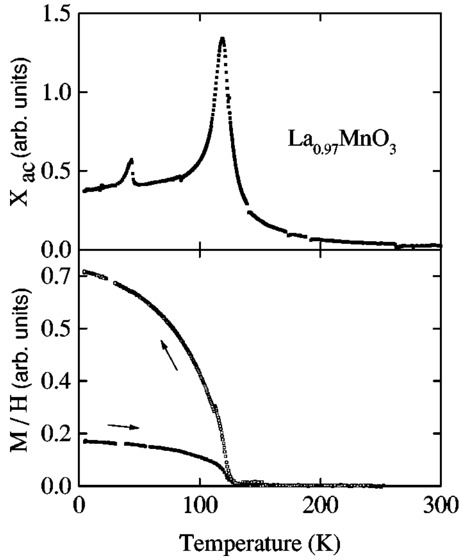

FIG. 3. Temperature dependence of the magnetic susceptibility in $La_{0.97}MnO_3$. Upper part: ac susceptibility; lower part: dc susceptibility in a field of 5 mT (zero field cooling and field cooling curves).

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 300 until 150 K (Fig. 2), which suggests that a mean field approach is correct. The effective moment deduced from a Brillouin fit is $\mu_{\mathrm{eff}} = 6.0\mu_B$. For this concentration also, clusters are present. The calculated mean field ordering temperature is $T_P = 114$ K, a value very close to the observed transition temperature ($T_C = 118$ K).

IV. ELECTRIC TRANSPORT

Both samples remain insulating (Fig. 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 resistance. The resistance as a function of field has a

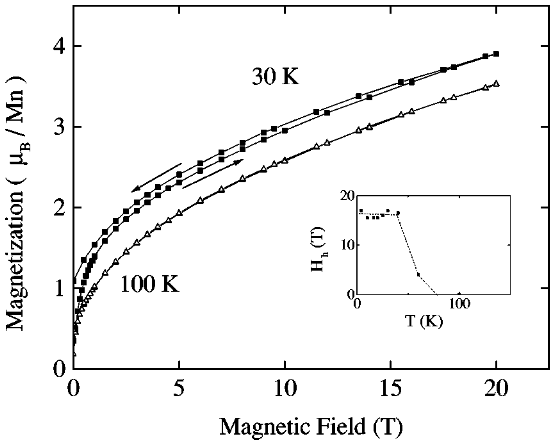

FIG. 4. Field dependence of the magnetization in $La_{0.97}MnO_3$. Inset: Hysteresis field H_h as a function of temperature.

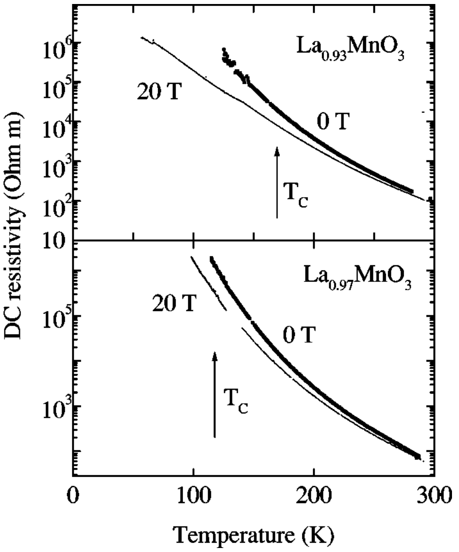

FIG. 5. Temperature dependence of the electrical resistivity in $La_{0.93}MnO_3$ and $La_{0.97}MnO_3$ without and with a 20 T magnetic field.

smooth variation for both samples. When the electric resistivity ρ is plotted as a function of the magnetization M, quite different behaviors 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 Fig. 6). Measurements were restricted to $T\geqslant 120$ K because of the high resistivity. At 120 K, 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 Goodenough.[22] $LaMnO_3$ involves Mn^{+3} ions in the $t_{2g}^3e_g^1(S=2)$ 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.

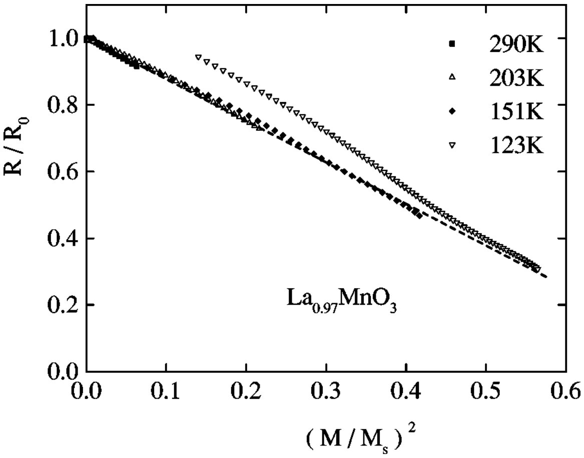

FIG. 6. Resistivity as a function of magnetization for $La_{0.97}MnO_3$.

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 $t_{2g}^3e_g^0(S=3/2)$ 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}^3 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 θ_{ij} is expressed by[12] $t_{ij}=b_{ij}\cos(\theta_{ij}/2)$. This introduces a canting of the spin; θ increases with Mn^{4+} content until complete ferromagnetism is reached,[9] around $x\simeq 0.3$. The canted state is characterized by a spontaneous magnetization M_s which is related to the canting angle θ:

$$M_s=I\cos(\theta/2) \tag{1}$$

$$\cos(\theta/2)=bx/4|J|S^2, \tag{2}$$

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

$$\chi_\perp=I^2/4|J|\gamma_0S^2N. \tag{3}$$

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 γ_0 the number of their neighbors in the adjacent layers $(\gamma_0=2)$.

The above features have been derived by de Gennes[9] assuming a pure canted spin arrangement, such that the spins form two sublattices separated by an angle θ. However, Inoue and Maekawa[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 θ 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 $\theta, 2\theta, 3\theta, \ldots,$ 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 de Gennes should not be substantially affected whether the spin arrangement is of the pure canting or spiral type.

Wollan and Koehler[5] have reported evidence for pure canted spins at low concentration. Their data agree with Eq. (2). Our experimental results for $La_{0.97}MnO_3$ agree quite well also with such a picture: the magnetization curves 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 $\chi \approx 1.74\times 10^{-2}$ SI we can estimate the antiferromagnetic coupling, using the average value for $S(S=1.96) J \approx -4.0$ K≈ -0.36 MeV. This value should be compared to the one deduced from spin wave measurements: in pure $LaMnO_3$, $J\approx -0.58$ MeV,[24,25] in $La_{0.95}Ca_{0.05}MnO_3$, it is reduced to $J\approx -0.38$ meV,[18] and in $La_{0.95}Ca_{0.05}MnO_3$, to $J\approx -0.28$ meV; in $La_{0.95}Sr_{0.05}MnO_3$, it is $J\approx -0.20$ MeV.[26] 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 ($r=0.122$ nm) and the one of calcium ions ($r=0.106$ nm). On the contrary, doping through strontium ions is different since its ionic radius is bigger ($r=0.126$ nm). The overlap of the oxygen and manganese orbitals is modified in a different way.

Using Eq. (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 $E_{d1}=-4bx \approx -104$ K and $E_{d2}=-2(b^2x^2/4|J|S^2)\approx -22$ K; 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 $E_{\mathrm{AF}}=2|J|S^2\cos\theta_0 \approx -20$ K. 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 $La_{0.95}Ca_{0.05}MnO_3, J'\approx 12$ K,[18] which leads to $E_F\approx -184$ K. In term of energy, the double exchange contribution has the same order of magnitude as the antiferromagnetic contribution (-22 K and -20 K, 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 $La_{1-x}Ca_xMnO_3$.[9] This confirms the great similitude between $La_{1-\delta}MnO_3$ and this system, in term of exchange interactions at least.

At low temperature, a high field hysteresis is present below 80 K (see Fig. 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.

de Gennes[9] 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: $k_BT_C=k_BT_P=\frac{2}{3}[(2|J|+4J')S^2-\frac{4}{5}]$, where J' takes into account the modification arising from the Zener carrier (J' increases with x as has been observed in Ref. 18). Taking the values determined above for J, J' and b, we get $T_C=T_P\approx 130$ K. Experimentally, we do observe $T_C\simeq T_P$ with a slightly smaller value (114 K). The treatment by 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 $\mu_{\mathrm{eff}}=6.0\mu_B$ 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_i. Temperature effects are only visible close to T_C: the mean field parameter starts decreasing for $T\leqslant 1.2T_C$. This reflects the onset of fluctuations.

What is the origin of these clusters? In these materials, presence of polarons has been detected.[12,16–18] 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 $La_{0.66}Ca_{0.33}MnO_3$,[17] it occurs below $1.8T_C$ and is accompanied by the formation of magnetoelastic 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 1.2 nm. 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 magnetoelastic interaction which is responsible for its formation is much stronger. This polaronic effect depends on the doping concentration. In $La_{1-x}Ca_xMnO_3$, Billinge *et al.*[16] 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 as the others do 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 $La_{1-\delta}MnO_3$ than in $La_{1-x}Ca_xMnO_3$.

Several theoretical treatments of the polaronic effects have been proposed. Millis, Shraiman, and Mueller[13] 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. Röder, Zhang, and Bishop[14] 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 $La_{0.66}Ca_{0.33}MnO_3$.[17] This lattice polaron picture remains controversial: Varma[15] 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 concern 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 de Gennes,[9] the same magnetic behavior is expected both for long range order or bound states. In a sample with the same doping level, Hennion *et al.*[18] have observed, at low temperature, magnetic droplets with a mean magnetization different from the matrix. 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 $La_{1-\delta}MnO_3$ than in $La_{1-x}Ca_xMnO_3$. The magnetic order is affected: $La_{0.97}MnO_3$ has a canted structure with $\theta \simeq 130°$, while $La_{0.92}Ca_{0.08}MnO_3$ is antiferromagnetic ($\theta \simeq 170°$).[18] 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[18] and none for the latter.[26] 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 $\rho(M):\rho(M)/\rho(0) = C(M/M_s)^2$ with $C \simeq 1.25$ (see Fig. 6). Such a law has been predicted by Furukawa.[27] 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.[28] 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 $La_{1-x}Sr_xMnO_3$ (Ref. 19) where the vale of C is about 4 for $0.15 \leqslant x \leqslant 0.2$, 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 4 K), 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 50 K even in high magnetic field. A similar ferromagnetic insulating phase has been observed in $La_{0.90}Sr_{0.10}MnO_3$ (Ref. 29) and in $LaMnO_{3.13}$.[22] 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,[30] 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 Allub and Alascio.[31] They have looked at the effect of localized states introduced by disorder. Their model was successful to account for the change in resistivity in $La_{1-x}Sr_xMnO_3$ (Ref. 19) where the system is ferromagnetic and insulating for $x < 0.125$. In $La_{1-\delta}MnO_3$, 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,[16,17] 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 fully 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 Töpfer and co-workers[21] in $La_{1-\delta}Mn_{1-\delta}O_3$. 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 $La_{1-\delta}MnO_3$ series, the occurrence of a ferromagnetic metalliclike phase is reduced as a function of the Mn^{4+} content compared 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 $Pr_{1-x}Ca_xMnO_3$.[32] Here, an additional process is involved: charge ordering occurs.

VI. CONCLUSIONS

We have studied the magnetic and electric properties of $La_{1-\delta}MnO_3$ for two values of δ: $\delta=0.03$ 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 ($\theta \simeq 130°$ and $T_C = 118$ K). Its magnetic behavior fits quite well with de Gennes theory of canted spins. We have extracted the values of the double exchange interaction ($b \approx 290$ K) and the antiferromagnetic indirect exchange ($J \approx -4.0$ K). In the paramagnetic regime, magnetoelastic polarons are present with an effective moment of $\mu_{\mathrm{eff}}=6.0\mu_B$. Their size is not affected by temperature for $1.2T_C<T<2.5T_C$, or by magnetic field ($B<20$ T) contrary to what is observed in the metallic ferromagnet $\mathrm{La_{0.66}Ca_{0.33}MnO_3}$. For higher vacancy content, $\delta=0.07$, polarons are still present but smaller in size; their effective moment is $\mu_{\mathrm{eff}}=5.8\mu_B$. The system becomes fully ferromagnetic thanks to double exchange, but the compound remains insulating, even in the ferromagnetic phase.

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