Pressure and magnetic-field effects on charge ordering in $La_{0.9}Sr_{0.1}MnO_3$

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Transport measurements under pressure and magnetic field on low-doped $La_{0.9}Sr_{0.1}MnO_3$ single crystals have clearly evidenced the *stabilization* of the low-temperature charge ordered state when increasing pressure and field. The observation of a pronounced change of magnetization, fastly increasing above a certain field threshold, accompanied by an enhancement of the resistivity indicates the presence of a strongly coupled magnetic and structural transformation. [S0163-1829(98)03723-0]

The rich variety of properties of $La_{1-x}Sr_xMnO_3$ oxides relies on the competing balance between three energy scales, namely, the Jahn-Teller (JT) nature of the Mn^{3+} ions and so the electron-phonon coupling, the kinetic energy associated with the carrier delocalization leading to ferromagnetic double-exchange coupling and a metallic state, and finally the Coulomb interaction producing a charge localization and eventually ordering. The balance among these energy sources can be varied by band filling (x) and bandwidth W control. Particularly, for low filling, the JT and charge localization become prominent whereas the metallic state is somewhat hampered.[1]

In fact, in $La_{1-x}Sr_xMnO_3$, for doping rates near $x=0.125$ three characteristic transition temperatures, occurring at $T_S \approx 260$ K, $T_C \approx 180$ K, and $T_{CO} \approx 150$ K have been identified.[2] They correspond, respectively, to (a) the temperature where the high-temperature dynamic Jahn-Teller distortion becomes static and an orbital ordering is established, (b) the onset of ferromagnetic and metallic state, and (c) the temperature where carriers become localized and thus the resistivity strongly increases. The nature of the low-temperature state has been described by Yamada *et al.*[3] who showed that charge localization is accompanied by ordering of polarons. Neutron diffraction experiments have also revealed that T_{CO} coincides with the appearance of some magnetic canting.[2] Similar behavior has been found for $x=0.1-0.165$ crystals although with different values of the transition temperatures.[1–6]

Charge ordering at low temperature has also been observed at higher band filling fractions ($x=\frac{1}{4}, \frac{1}{3}, \frac{1}{2}, ..$).[7–9] It has been shown that T_{CO} can be *suppressed* either by applying a magnetic field (H) or hydrostatic pressure (P). Particularly, for $Pr_{1/2}Ca_{1/2}MnO_3$, $d \ln T_{CO}/dP \approx -0.05\ GPa^{-1}$ and $d \ln T_{CO}/dH \approx -0.007\ T^{-1}$.[9] This behavior can be understood in terms of effective bandwidth enhancement and thus the stabilization of the ferromagnetic (F) metallic state in front of the charge-ordered (CO) insulating one. Interestingly enough, recent measurements on $La_{0.88}Sr_{0.12}MnO_3$ (Ref. 5) have shown that for this low-doped material, the charge-ordering temperature T_{CO} *rises* with pressure. That would imply that the CO state is favored and the F state occurring at a higher temperature is unstable under pressure. Of course, suppression of the F state under pressure is opposite to what has been observed[10,11] and thus the reported positive dT_{CO}/dP merits further experiments.

In this paper, we address the question of the relative stability of the CO and F phases at low doping ($x=0.1$) under pressure and magnetic field. It is found that CO is stabilized under pressure or field and thus T_{CO} *rises* with P and H. Magnetization and transport data provide insight into the nature of this phase transition.

Single crystals of $La_{1-x}Sr_xMnO_3$ with $x=0.10$ were grown by floating-zone method with radiation heating without crucible. They were cut into $0.5\times0.5\times1\ mm^3$ bars for transport and magnetic measurements. The crystals are found to be twinned. Resistivity measurements were done under a quasihydrostatic pressure by using a clamp-type piston cylinder cell with an organic liquid as a pressure transmitting medium. The decrease of pressure when cooling was taken into account. Electrical contacts to each sample were made by using graphite paste and resistance was measured by the conventional dc four-probe method. It is found that the low-temperature resistivity is about $6\times10^3\ \Omega$ cm, in agreement with previous reports on crystals of similar composition. However, due to the significant size of the contacts relative to the crystal size, accurate determination of the resistivity is difficult; for this reason we will only present the measured resistance values. Field-dependent resistance and magnetization up to 5.5 T were measured using a commercial superconducting quantum interference device system.

In Fig. 1, the temperature dependence (heating process) of the resistance $R(T)$ is presented. The temperatures $T_S \approx 320$ K, $T_C \approx 145$ K, and $T_{CO} \approx 127$ K can be clearly appreciated. The shape of $R(T)$ and the characteristic temperatures are in agreement with those reported by Urushibara *et al.*[1] Both T_{CO} and T_S are hysteretic revealing the first-order nature of the corresponding transitions. Figures 2 and 3 show the resistance vs temperature under various pressures and magnetic fields, respectively. Inspection of the data of Fig. 2 immediately reveals that both T_C and T_{CO} temperatures rise under pressure. Positive $dT_C/dP\ (+2.3\ K\ kbar^{-1})$ (Fig. 2 inset) is in agreement with results obtained for higher

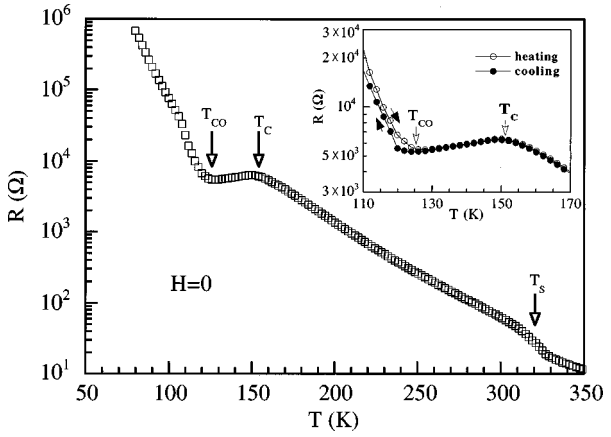

FIG. 1. Temperature dependence (heating) of the resistance $R(T)$ for a $La_{0.9}Sr_{0.1}MnO_3$ single crystal. Inset: magnification of the $T_C - T_{CO}$ temperature region. The thermal hysteresis is clearly visible.

doped materials ($x > \frac{1}{3}$) (Ref. 10) where it has been shown that it reflects basically the bandwidth broadening under pressure.[11] However, the observation of positive dT_{CO}/dP (≈ 2.5 K/kbar) is in sharp contrast with results reported for higher filled band materials ($x \geq 0.15$) (Refs. 5 and 9) where it has been found that T_{CO} decreases under pressure. In agreement with the present data, positive dT_{CO}/dP ($+1.45$ K/kbar) has also been very recently reported for $x = 0.12$.[5] It should thus be concluded that for low doping, the charge-ordered insulating state occurring below T_{CO} becomes favored under pressure and thus the low-temperature part of $\rho(T)$ shifts towards higher temperature.

On the other hand, the field dependence of $R(T)$, shown in Fig. 3, also displays the very same trend, namely, when

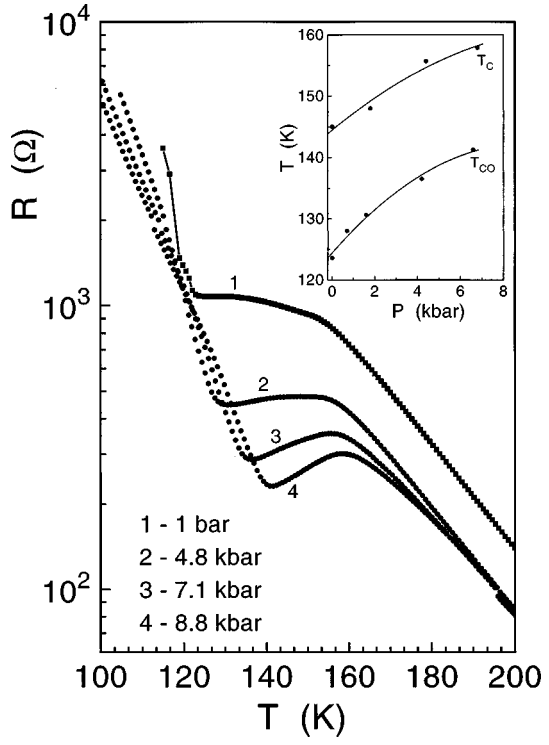

FIG. 2. Resistance $R(T)$ (heating) under various pressures. Inset: pressure dependencies of T_C and T_{CO}.

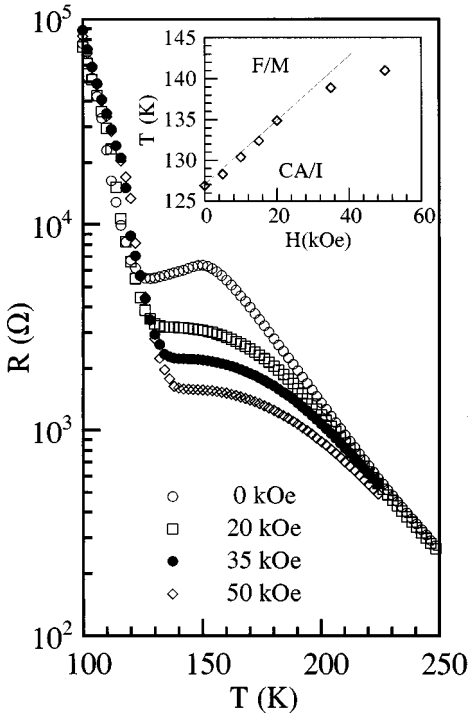

FIG. 3. Resistance $R(T)$ (heating) under various fields. Inset: field dependence of T_{CO}.

increasing the field T_{CO} rises at a rate $+0.4$ K/kOe (Fig. 3 inset). Thus, the effects of field and pressure on T_{CO} seem to be equivalent, with 1 kbar roughly corresponding to 6.2 kOe.

Detailed inspection of the $R(T)$ curves as a function of the applied field (Fig. 3) reveals a very remarkable feature, such as the existence of a narrow range of temperatures, below $T_{CO}(H=0)$, in which the resitivity increases with field, i.e., a temperature region of positive magnetoresistance (see Fig. 4). Nevertheless, for $T > T_{CO}(H=0)$ the usual negative magnetoresistance is recovered. This interesting behavior is clearly evidenced in Fig. 4, where the magnetoresistance (MR) defined as $[R(H) - R(H=0)]/R(H=0)$ is depicted in the temperature region of interest. A well-defined region of positive MR can be observed. The negative MR occurring at a higher temperature is the conventional result and not of interest here. Thus, data of Figs. 2 and 3 show that

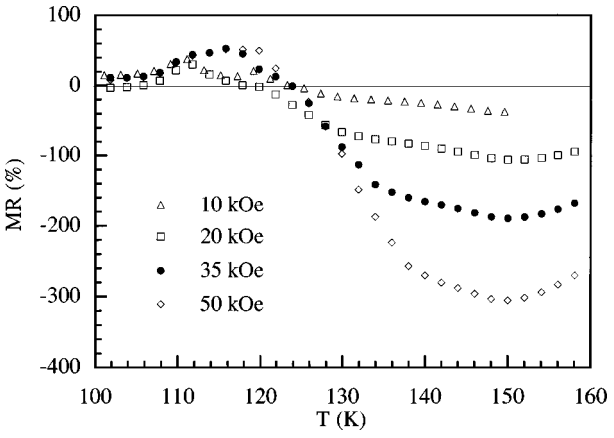

FIG. 4. Magnetoresistance$=[R(H) - R(H=0)]/R(H=0)$ vs temperature.

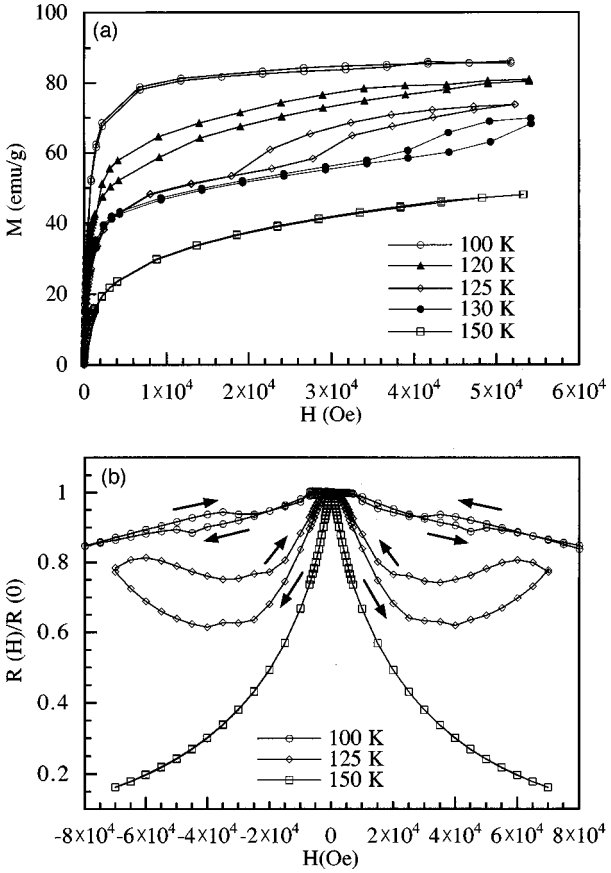

FIG. 5. Magnetization $M(H)$ loops (a) and resistance vs field loops $R(H)/R(0)$ (b) obtained at several temperatures.

in the temperature range (127–100 K), where the transition from the ferromagnetic/metallic (F/M) to the canted/insulating (CA/I) state occurs, the low-temperature state is stabilized by applying a magnetic field as well as applying hydrostatic pressure.

This observation is somewhat unexpected and deserves further experiments. In order to get insight into the nature of this field-induced phase transition we present in Fig. 5(a) the $M(H)$ loops obtained at several temperatures around T_{CO}. Whereas at temperatures well above and below $T_{CO}(H=0)$ the $M(H)$ curves are featureless and archetypal for the magnetization process, the loops recorded at 125 K, that is, close to $T_{CO}(H=0)$, display a remarkable jump of magnetization at $H=20$ kOe before approaching saturation. The hysteretic behavior is also evident in the descending branch of the loop. We note that the threshold field at which the magnetization suddenly increase, rises from ≈ 2 kOe at 120 K to ≈ 30 kOe at 130 K. Similar open loops are observed at any temperature in the 110–130 K range, which corresponds to the temperature interval where positive magnetoresistance has been found. The observed feature is a signature of a field-induced magnetic transition. More illustrating is the resistance vs field loops shown in Fig. 5(b). At 125 K, when raising the field there is an initial fast drop of resistance, followed by a field region of positive magnetoresistance. The retreating branch of the loop is always of higher resistivity. Comparison of Figs. 5(a) and 5(b) clearly reveals that when increasing the field above 20 kOe a sudden transition to a state of higher magnetization *and* resistivity occurs. We stress that

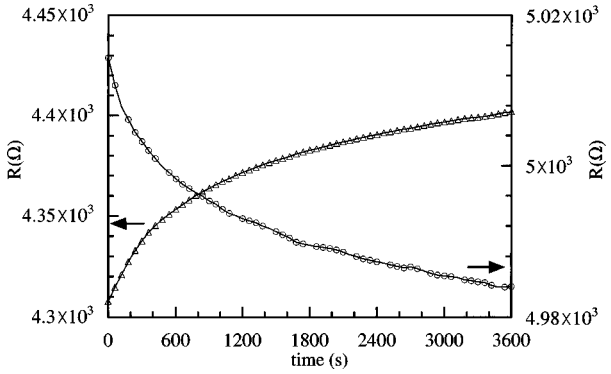

FIG. 6. Time dependence of the resistance $R(t)$ at 125 K and 40 kOe, measured in the increasing (triangles) and decreasing (circles) branches of the field loop.

this behavior is clearly different from the conventional magnetoresistance observed at higher temperature [i.e., 150 K; Fig. 5(b)] where MR is clearly negative in all field ranges.

Therefore, data of Fig. 5 reveal that above a threshold field (≈ 20 kOe at 125 K) indeed there is a phase transition towards a state having a *higher* magnetization and *larger* resistivity. The hysteretic behavior observed in Fig. 5 reflects the existence of metastable states that tend to relax with time. These relaxation processes are illustrated in Fig. 6 where we show the time-dependence $R(t)$ at $T \approx 125$ K for an applied field of 40 kOe. As can be appreciated in the figure, the relaxation takes place in opposite directions [increasing field (triangles) and decreasing field (circles)] depending on in which branch of the hysteresis loop the sample is. Of course the relaxation disappears for higher temperatures as does the hysteretic $M(H)$ behavior.

We have presented a complete set of experimental data that reveal that field and pressure can induce a transition from the ferromagnetic metallic state towards the insulating canted magnetic state. We note that the canted magnetic state has a larger magnetization than the ferromagnetic one at a similar temperature. In fact magnetization vs temperature curves recorded at $H=5$ kOe display a pronounced enhancement of magnetization at $T \approx 120$ K (Fig. 7). We note that the measured magnetization at 5 K corresponds to 3.5 μ_B/Mn ion. The same trend can be also observed in the low-field (50

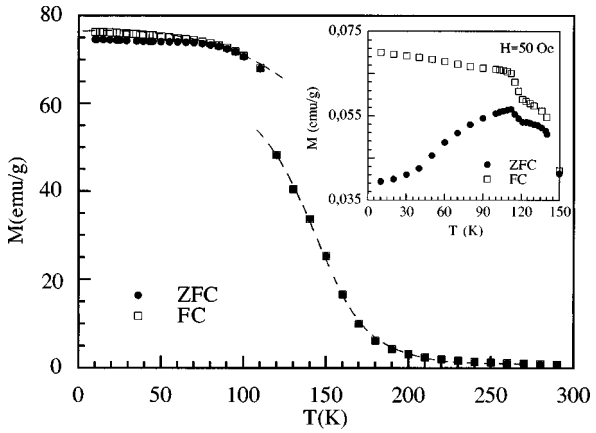

FIG. 7. Magnetization $M(T)$ curves recorded at $H=5$ kOe. Inset: Low-field (50 Oe) magnetization data. Open and solid symbols correspond to field cooling (FC) and zero field cooling (ZFC) experiments, respectively.

Oe) magnetization data shown in Fig. 7 inset.

These experimental results are concisely described by the following picture. Consider the H-T phase diagram shown in Fig. 3 inset, constructed from the $R(T)$ curves under the field and using the minimum of $R(T)$ to define $T_{CO}(H)$. This line separates the CA/I state from the F/M one. In a typical $M(H)$ run at $T \geqslant T_{CO}$, i.e., starting from the F/M state, when raising the field the magnetization rises and the MR initially is negative; when crossing the $T_{CO}(H)$ line, the magnetization jumps to larger values and the resistivity also increases. Across this first-order transition, hysteresis in both magnetization and resistivity is observed. Similarly, in a constant-field magnetization vs temperature measurement, when crossing the $T_{CO}(H)$ line the magnetization increases.

The observation of a remarkable magnetization enhancement in the insulating phase is somewhat unexpected as has been reported that in zero field, the low-temperature state is a canted ferromagnet.[2] Unless the Curie temperature of this canted phase (we recall here that it occurs at T_{CO} where significant changes in the Mn-O bonds take place) is much larger than the Curie temperature of the ferromagnetic phase (T_C) and thus at 120 K the reduced magnetization is larger, the data of Fig. 7 would imply a moment enhancement. According to the previous picture the magnetic moment per Mn atom would increase when crossing the $T_{CO}(H)$ line; while neutron diffraction experiments could give a definitive answer to this suggestion it can be speculated that moment enhancement in the insulating phase or under field can be understood if one assumes that in the F/M phase the polarization of the conduction band is not complete, that is, the Fermi level crosses the spin-up and spin-down subbands. Opening a gap in the spin-up and spin-down bands in the insulating state or band shift under a magnetic field could result in a spin transfer from the minority-spin subband to the majority one thus leading to a higher moment. Recent experiments in the $\frac{1}{3}$-filled oxide $La_{2/3}Sr_{1/3}MnO_3$ have shown that the polarization of the e_g band is of about 80%.[12] That means that at the Fermi level there is a partial overlapping of the spin-up and spin-down subbands. It is reasonable to expect that at lower filling ($x=0.1$), that is, rising Fermi level, the polarization of the conduction band is to be lowered.

On the other hand, application of pressure should decrease sample orthorhombicity by reducing Mn-O-Mn bond bending and simultaneously reducing any difference among Mn-O bond length. Under such circumstances it is clear that the low-temperature CA/I state should be favored as in this phase the neutron diffraction experiments have shown that orbital ordering is completely suppressed and the Mn-O bond lengths become equal.[2] In fact, the same reason is responsible for the lowering of the T_S transition under pressure. We recall here that at $T>T_S$ the dynamic Jahn-Teller effect leads also to the absence of orbital ordering and thus all bond distances are also very similar.[2] In fact, dT_S/dP has also been found to be negative in $La_{0.835}Sr_{0.165}MnO_3$ due to the reduction of the Mn-O-Mn bond bending under pressure at the concomitant stabilization of rhombohedral phase in front of the orthorhombic one observed at $T<T_S$.[4]

In summary, transport measurements under pressure and magnetic field have clearly evidenced the stabilization of the low-temperature charge-ordered state in low-doped manganites. This behavior is sharply distinct from the reported melting of the hole sublattice ($\frac{1}{2}$ band filling) under field. Observation of a pronounced change of magnetization, fastly increasing above a certain field threshold, accompanied by an enhancement of the resistivity indicates the presence of a strongly coupled magnetic and structural transformation. The remarkable observation of a higher magnetization at $T<T_{CO}$ could signal a change of the polarization of the conduction band.

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[1] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14 103 (1995).

[2] L. Pinsard, J. Rodríguez-Carvajal, A. H. Moudden, A. Anane, A. Revcolevschi, and C. Dupas, Physica B **234–236**, 856 (1997).

[3] Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami, and S. Katano, Phys. Rev. Lett. **77**, 904 (1996).

[4] K. Kamenev, G. Balakrishnan, M. R. Lees, D. McK. Paul, Z. Arnold, and O. Mikulina, Phys. Rev. B **56**, 2285 (1997).

[5] J.-S. Zhou, J. B. Goodenough, A. Asamitsu, and Y. Tokura, Phys. Rev. Lett. **79**, 3234 (1997).

[6] Y. Moritomo, H. Kuwahara, Y. Tomioka, and Y. Tokura, Phys. Rev. B **55**, 7549 (1997).

[7] Z. Jirak *et al.*, J. Magn. Magn. Mater. **15–18**, 519 (1980).

[8] H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **78**, 4253 (1997), and references therein.

[9] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, Phys. Rev. B **53**, R1689 (1996).

[10] Y. Moritomo *et al.*, Phys. Rev. B **51**, 16 491 (1995); H. Y. Hwang *et al.*, *ibid.* **52**, 15 046 (1995); J. J. Neumeier *et al.*, *ibid.* **52**, 7006 (1995).

[11] V. Laukhin, J. Fontcuberta, J. L. García-Muñoz, and X. Obradors, Phys. Rev. B **56**, R10 009 (1997).

[12] M. Viret, M. Drouet, J. Nassar, J. P. Contour, C. Fermon, and A. Fert, Europhys. Lett. **39**, 545 (1997).