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Nonlinear electrical response in a non-charge-ordered manganite: $Pr_{0.8}Ca_{0.2}MnO_3$

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Up to now, electric-field-induced nonlinear conduction in the $Pr_{1-x}Ca_xMnO_3$ system (PCMO) has been ascribed to a current-induced destabilization of the charge ordered phase. However, for $x \leqslant 0.25$, a ferromagnetic insulator state is observed, and charge ordering (CO) is absent whatever the temperature. A systematic investigation of nonlinear transport in the ferromagnetic insulator $Pr_{0.8}Ca_{0.2}MnO_3$ shows rather similar results to those obtained in charge-ordered systems. However, the experimental features observed in $Pr_{0.8}Ca_{0.2}MnO_3$ are distinct in that the collapse of the CO energy gap cannot be invoked as is usually done in the other members of the PCMO system. We propose interpretations in which the effectiveness of the double exchange is restored upon application of an electric field.

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Hole-doped perovskite manganese oxides $R_{1-x}A_xMnO_3$ (R and A being trivalent rare-earth and divalent ions, respectively) are associated with a wide variety of electronic and magnetic properties depending on the value of x and the averaged A-site cation radius, $\langle r_A \rangle$.[1] These materials have recently been the subject of intense studies due to intriguing phenomena such as charge/orbital ordering (CO)[2] or colossal magnetoresistance.[3] The latter is usually interpreted by means of the double-exchange (DE) interaction scenario[4] which gives an interesting qualitative interpretation of coupled ferromagnetic ordering and metallicity. Within such a framework, the ferromagnetic (FM) ordering is related to a large electronic itinerancy, i.e., a metallic behavior. Among the various mixed-valent manganites studied so far, the $Pr_{1-x}Ca_xMnO_3$ system (PCMO) is perhaps the most interesting because it shows a great variety of ordered phases that are very sensitive to cation/anion doping.[5–11] For $0.3 \leqslant x < 0.8$, charge ordering of Mn^{3+} and Mn^{4+} (CO) is found and an antiferromagnetic (AF) ordering can be observed with Néel temperatures ranging from 100 to 170 K for $x = 0.8$ and 0.3, respectively. Due to its low tolerance factor, this system happens to remain insulating, giving rise, under zero field, to a charge-ordered insulating state (COI). It has been widely shown that this COI state in the PCMO system can be melted into a metallic ferromagnet (FMM) upon application of a magnetic field of sufficient amplitude.[6,8,12–15] Within the doping range $0.3 \leqslant x \leqslant 0.5$, in addition to the magnetic field, such a destabilization of the COI state can also be induced by external perturbations such as irradiation by x ray[16] or light,[17,18] and application of pressure[19] or electric field.[20–25] Those optical or irradiation induced transitions are usually argued to be a result of classical percolation transport in a nonhomogeneous medium; however, the role of the application of an electric field is not so clear.

For instance, Guha and co-workers[22,23] found that the current-induced destabilization of the COI state in $Pr_{0.63}Ca_{0.37}MnO_3$ leads to a regime of negative differential resistivity (NDR) ($dV/dI < 0$) with a concomitant enhancement of magnetization. The authors invoke a the creation of low-resistivity conducting paths made up of FM phases along the current flow. Very recently, Yuzhelevski *et al.*[26] claimed, in a low doped $La_{1-x}Ca_xMnO_3$ (LCMO) system, that the influence of light, x ray, and current may be interpreted in terms of spin-polarized tunnel conduction mechanism modifying phase separation conditions along the percolation path.

Up to now, all experiments investigating the effect of electric field on the conducting behavior of the PCMO system have mostly been carried out on CO candidates. Consequently, interpretations based on multiphase coexistence (AF-COI and FMM phases whose respective volumes in the bulk are modified under perturbations) is often raised.[17,18,20–23] The very low doping regime of the PCMO system has not been explored yet. For $x \leqslant 0.25$, a ferromagnetic insulator (FMI) state is found, and charge ordering is not observed whatever the temperature. Moreover, a metallic state is never realized, even upon application of a magnetic field. This can be understood as follows: on the one hand, for this system we have an important inward tilt of the Mn^{3+}-O-Mn^{4+} bounds which results in a decrease of the $d_{z^2} - p\sigma - d_{z^2}$ overlaps. This produces a decrease of the magnitude of the e_g bandwidth and, consequently, a reduction in the effectiveness of the double exchange. On the other hand, for $x \leqslant 0.25$ we deal with a very low hole concentration which does not favor a delocalized electronic state.

The aim of our experience was to investigate whether a current-induced metal-insulator transition can be observed in a non-CO manganite of the PCMO system. For this purpose, a crystal of $Pr_{0.8}Ca_{0.2}MnO_3$, not so far from the CO region, has been chosen. Although a metal-insulator transition has not been clearly observed, the resistance for increasing bias current is drastically reduced. Moreover, a strong nonlinear electrical conduction is found with a NDR developing for $T < T_c$. This behavior is not sensitive to the application of a magnetic field. Compared to already reported results, the experimental features observed here are distinct in that the collapse of the CO energy gap can not be invoke as is usually done in the other members of the PCMO system.[17,18,20–25]

Using the floating-zone method with a feeding rod of nominal composition $Pr_{0.8}Ca_{0.2}MnO_3$, a several-cm-long single crystal was grown in a mirror furnace. Two samples were cut out of the central part of this crystal, one of them for resistivity measurements and the other for magnetization

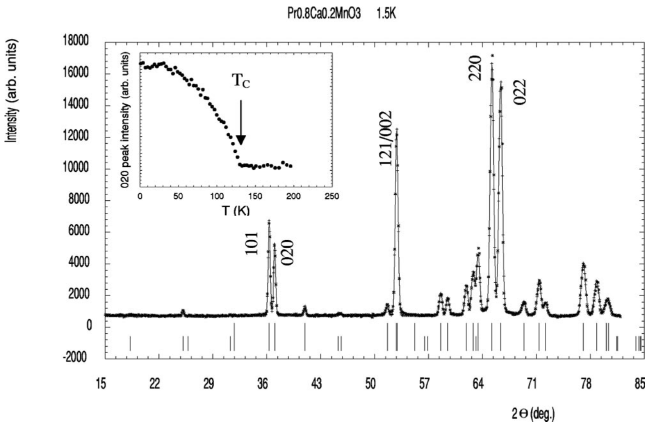

FIG. 1. 1.5-K neutron diffraction patterns: continuous line for calculated plot, stars for experimental data; the upper Bragg strikes correspond to the *Pnma* crystallographic structure and the lower one to the magnetic phase. The main indexations are also given. Inset: 020 FM peak intensity vs temperature.

and specific-heat measurements. X-ray-diffraction and electron-diffraction studies, which were performed on pieces coming from the same part of the crystal, attested that the samples are single phased, and well crystallized. The cell is orthorhombic with a *Pnma* space group, in agreement with previously reported structural data. The energy dispersive spectroscopy analyses confirm that the composition is homogeneous and close to the nominal one, in the limit of the accuracy of the technique. The electron-diffraction characterization was also carried out versus temperature, from room temperature to 90 K. The reconstruction of the reciprocal space showed that the cell parameters and symmetry remain unchanged in the whole domain of temperature and, more especially, no extra reflections have been detected. This electron-diffraction observation, coupled with lattice imaging, shows that, in our sample, there is no charge ordering effect, even at short-range distances. All x-ray- and electron-diffraction observations agree with previous published results for compounds of the same system.[11]

In order to characterize the magnetic structure of the sample, we have performed a temperature dependence of the diffraction patterns on the *G*4.1 neutron spectrometer ($\lambda = 0.2426$ nm) on the Orphee source (LLB-Saclay, France) in the 2.00–81.90 2θ angular range. The sample was first powdered, and the diffracted spectra were recorded as function of temperature from 300 K down to 1.5 K. For $T < T_c$, the data were fitted with a *Pnma* structure with a ferromagnetic order with the Mn spins aligned along the *a* axis with a resolution-limited correlation length (more than 100 nm). The saturated moment is $3.46(4)\mu_B$/Mn at 1.5 K and the Curie temperature is around 135 K. No evidence of any antiferromagnetic peak was observed in this sample down to 1.5 K. The 1.5 K experimental and calculated patterns given in Fig. 1 test the validity of the fit. The 020 peak intensity versus temperature (see the inset) shows the FM component evolution and allows a determination of T_c. A magnetic contribution was also added for Pr in the calculation at lower temperatures.

Four linear contact pads of In were soldered onto the sample in linear four-probe configuration. *V*-*I* data were taken with current biasing (Keithley 236) and with a temperature control of 100 mK. The measurements under magnetic field were done using a superconducting magnet capable of producing 9 T.

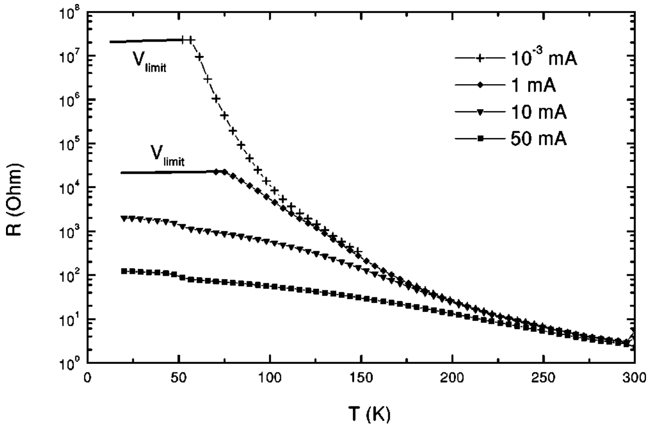

FIG. 2. Temperature dependence of resistance for a $Pr_{0.8}Ca_{0.2}MnO_3$ crystal with various bias currents.

In Fig. 2, we show the temperature variation of the resistance ($R = V/I$) of a $Pr_{0.8}Ca_{0.2}MnO_3$ crystal for various bias current $R_I(T)$ under zero field. When the current is small (10^{-3} mA and 1 mA), the sample shows an insulating behavior and, at low temperature, the large resistance increase overloads our current source. Our current source overloads for 100 V, thus the maximum resistance that we can measure for 10^{-3} is around 100 MΩ. For higher currents (10 and 50 mA), the resistance is strongly depressed with a trend to saturation when the temperature is lowered. We do not see a clear metal-like decrease in resistance below T_c, and the observed behavior is rather similar to that of $Gd_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Ca_{0.5}MnO_3$ films deposited on La_2O_3 (LAO) (Ref. 24) and PCMO crystals.[22,23] The latter papers report that electrical current triggers the collapse of the low-temperature electrically insulating CO state to a FMM state. Measurements of $R_I(T)$ have been carried out upon cooling and warming, and no hysteresis was observed. Around 50 K, a slight anomaly can be observed on every $R_I(T)$; this can be linked to the Pr magnetic ordering as observed by neutron experiments.

Figure 3 shows *V*-*I* characteristics in a semi-log scale for $T < T_c$ (80, 90, and 100 K) under zero field. The *V*-*I* characteristics for temperatures above the Curie temperature (170 and 300 K) are displayed in Fig. 4. For $T = 300$ K, an Ohmic conduction is observed on the whole current range. As one approaches T_c, nonlinear conduction sets in. As *T* is lowered below T_c the nonlinearity increases and the *V*-*I* curves exhibit a negative differential resistance. The region of NDR is observed when the bias current attains a current threshold (I_{th}). The latter is higher when the temperature is close to T_c from below, 0.4 mA at 80 K up to 2.5 mA at 100 K; the corresponding current densities are 0.02 and 0.19 A cm^{-2}, respectively. The data displayed in Figs. 3 and 4 are highly reproducible and do not show any significant hysteretic behavior when the bias current is cycled (5% at its maximum).

We have carefully checked that the Joule heating is irrel-

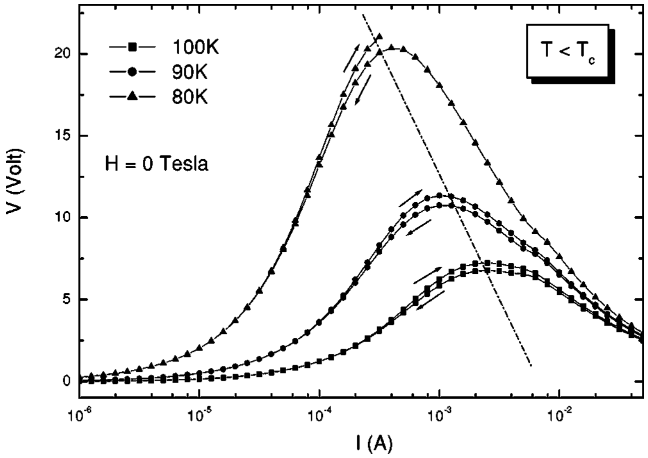

FIG. 3. *V-I* characteristics under zero field for temperatures below T_c (80, 90, and 100 K).

evant to account for this current-induced effect. The temperature rise of the sample with respect to the sample holder (ΔT) has been measured by attaching a thermometer on the top of the sample itself. We have obtained $\Delta T \leqslant 25$ K at the lowest temperature (80 K) and for the highest power dissipation level. In this low-temperature range, the power dissipation level where the NDR sets in leads to $\Delta T < 3$ K. For higher temperature of measurements, ΔT becomes negligible. Moreover, for these temperatures, the heat dissipation is low which may induce high Joule heating and possible nonlinear *V-I* characteristics. However, at 300 K, the *V-I* curve is linear over the whole current range. Finally, all these points confirm that the phenomenons observed above are not triggered by simple thermal effects or by heating of the crystal.

The *V-I* characteristics are not strongly modified under magnetic field. As an example, Fig. 5 shows measurements at 90 K with and without magnetic field. It can be observed that the NDR region sets in for rather close values of the current threshold.. The variation is not substantial enough to invoke a magnetic-field effect. To sum up, the main results are as follows. (i) The occurrence of a strong nonlinear conduction as one approaches T_c, leading to NDR when the temperature is lowered well below T_c. (ii) Nonhysteretic *V-I* characteristics upon cycling the bias current. (iii) No modification of the above features when a magnetic field is applied.

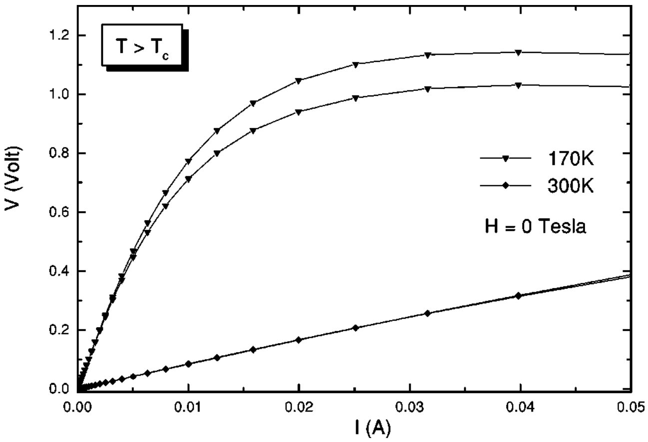

FIG. 4. *V-I* characteristics under zero field for temperatures above T_c (170 and 300 K).

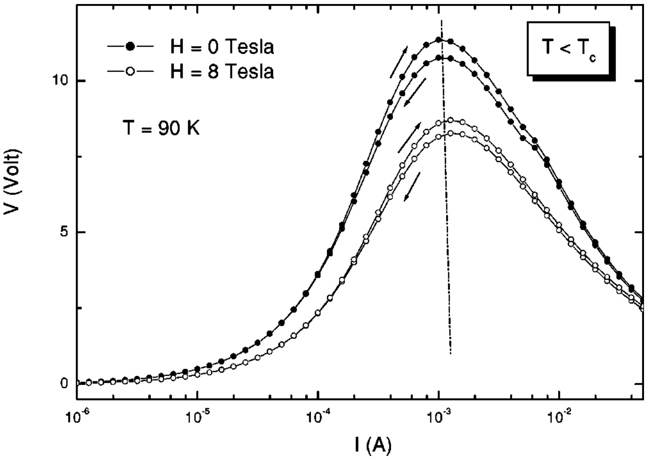

FIG. 5. *V-I* characteristics for $T = 90$ K under 0 and 8 T.

The zero-field data shown for $Pr_{0.8}Ca_{0.2}MnO_3$ are reminiscent of metal-insulator transition and nonlinear conduction induced by an electric field in the CO compounds of the PCMO system ($0.3 \leqslant x < 0.8$).[20–25] In the latter experiments, a melting of the CO state is usually invoked to account for this phenomenon. In the case of a current-induced transition, it is proposed that a breakdown of the CO state locally leads to the creation of metallic filaments made up of a FM phase when a current threshold is passing through the sample. The resistance drop and, concomitantly, the occurrence of NDR, are results of the current being drawn into the metallic conducting path forming a parallel circuit. Within such a scenario, the experimentally observed disappearance of the NDR upon application of magnetic field is explained by considering the magnetic-field-induced transformation of AFCOI state into FMM. The coexistence of a CO phase and a FM phase would prevent the nucleation of metallic filaments needed for the occurrence of NDR.[20,22]

Let us now turn to the data obtained for our weakly doped FMI $Pr_{0.8}Ca_{0.2}MnO_3$ crystal. As developed in Ref. 11 and on the basis of our neutron-diffraction data, charge ordering is never observed in $Pr_{0.8}Ca_{0.2}MnO_3$. Thus one can hardly invoke the electric-field-induced destabilization of the CO state to understand our experimental data. Our results suggest that for a sufficient bias current, a conduction path is opened. This conduction path is closely linked to the FM ground state of the sample, and the magnetic field does not trigger or limit this phenomenon. Moreover, the nonhysteretic nature of the *V-I* characteristics is not in favor of an electric-field-induced metastable state.

Although a theoretical understanding of the mechanisms at work in mixed-valent manganites is still incomplete, DE is commonly adopted as a main ingredient. In the completely ferromagnetic phase, e_g electrons of Mn^{3+} can hop coherently without magnetic scattering by t_{2g} spins, while they become strongly incoherent if the t_{2g} spins are disordered.

However, for ferromagnetic mixed manganites, localization effects can arise due to spatial fluctuations of structural and spin-dependent potentials, as discussed by Coey *et al.*[27] As emphasized above, in $Pr_{0.8}Ca_{0.2}MnO_3$, the important inward tilt of the Mn^{3+}-O-Mn^{4+} bonds results in a decrease of the e_g bandwidth. An electric field may induce a local electrical moment in the MnO_6 octahedra by modifying the spatial distribution of the charges. This leads to an increase of the d_{z^2}-$p\sigma$-d_{z^2} overlaps i.e., an increase of the e_g bandwidth. As a consequence, the hopping probability and the mobility of the carriers would be greatly enhanced. The magnetic ground state of $Pr_{0.8}Ca_{0.2}MnO_3$ is definitely ferromagnetic; thus there is no need of a magnetic field to initiate a DE-mediated hopping. The slight modification between the V-I curves with and without magnetic field could be explained as a field induced suppression of the deviation from perfect collinear ferromagnetism which implies a spin-only moment of $3.8\mu_B/\mathrm{Mn}$ [neutron-diffraction experiments give $3.46(4)\mu_B/\mathrm{Mn}$ for $H=0$ T]. Moreover, this scenario is supported by the temperature dependence of I_{th}. Indeed, the FM correlations are enhanced as the temperature is lowered well below T_c and smaller bias current threshold may be required to induce delocalization via DE.

The nonlinear conduction, and more particularly the NDR, can also arise as a result of inelastic tunneling. One can start off from this point by proposing another kind of process which could be at work in such a low-doped system. To do so, one could imagine a rather inhomogeneous material, magnetically speaking. In this scenario, due to the random distribution of the Mn^{3+} and Mn^{4+} ions, the long-range FM ordering may appear in spatially distinct, strongly topologically, disordered regions of the sample. In these regions the DE would be locally at work; however, metallicity could not be macroscopically observed because these regions,where the carriers are mobile, would be interrupted by tunnel-type weak links whose nature remains unclear. Twinning might be a clue; such disorder effects are unavoidable in crystals and could play the role of tunneling junctions between highly ferromagnetic domains. Thus the peculiar behavior observed in $Pr_{0.8}Ca_{0.2}MnO_3$ can be tentatively understood by considering a spin-polarized current flowing across twin-boundary tunnel junctions separating neighboring ferromagnetic domains.

In summary, we have carried out a systematic investigation of the nonlinear transport in the FMI $Pr_{0.8}Ca_{0.2}MnO_3$. Experimental data are rather similar to those obtained in charge-ordered systems. However, the ground state of $Pr_{0.8}Ca_{0.2}MnO_3$ prevents us from invoking a current-induced destabilization of the charge-ordered phase to account for experimental data. We propose interpretations in which the effectiveness of the DE is restored upon application of electric field.

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[1] For a review, see *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998); *Colossal Magnetoresistive Oxides*, edited by Y. Tokura (Gordon and Breach, New York, 1999).

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