Current switching effects induced by electric and magnetic fields in Sr-substituted $Pr_{0.7}Ca_{0.3}MnO_3$ films

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Measurements of electric- and magnetic-field-induced changes in electrical conduction indicate the coexistence of charge-ordered and ferromagnetically ordered regions in the Sr-substituted $Pr_{0.7}Ca_{0.3}MnO_3$ epitaxial films. Percolative, metal-like channels open up in this topologically inhomogeneous medium on the application of these fields, and a technologically promising orders-of-magnitude drop in resistance ensues. Measurements of current-voltage characteristics and the temperature dependence of resistivity show hysteretic and history effects, which are intimately linked to the relative stability of the two phases.

The physics of the phase transition from a charge-ordered (CO) antiferromagnetic to a charge-delocalized (CD) ferromagnetic state in $Pr_{1-x}Ca_xMnO_3$ and related compounds is of much current interest.[1–5] It has been observed that the CO state is unstable under a variety of external perturbations.[6–10] Asamitsu *et al.*[11] argued that the real-space ordering of the planes containing Mn^{3+} and Mn^{4+} ions in a charge-ordered manganite can be broken if holes are forced to move between them through the application of a strong electric field. Their measurements on $Pr_{0.7}Ca_{0.3}MnO_3$ bulk crystals at low fields showed a strongly insulating behavior below the charge-ordering transition temperature T_{CO}. The application of moderate to high electric fields ($E > 10^3$ V/cm), however, led to a precipitous drop in resistance at temperature below the Neel temperature T_N. Similar results have also been reported recently by Stankiewicz *et al.*[12] in ceramic samples of $Pr_{1-x}Ca_xMnO_3$ with $x = 0.33$ and 0.4. Interestingly, this drop in resistance is much larger than the well-known colossal magnetoresistance effect seen in ferromagnetic manganites near their Curie temperature.[13,14] The possibility of using a wide range of perturbations to realize this effect increases its technological potential considerably. Since miniaturization is a key requirement in all technologies, it is desirable to have these compounds in the form of thin films. Furthermore, the high-electric-field effects can be realized in thin-film samples at easily manageable voltages if a suitable constriction or heterostructure geometry is used. This has been demonstrated for the charge-ordered manganites of the exactly half-filled e_g band.[15]

Notwithstanding the technological significance of this spectacular increase in electrical conductivity, the phenomenon raises many fundamental questions about the stability of the CO state and the dynamics of the CO to CD transition under strong driving forces. In this paper we report our studies of electrical switching effects in epitaxial thin films of $Pr_{0.7}Ca_{0.27}Sr_{0.03}MnO_3$. We observe similar effects of electric and magnetic fields on charge transport in a temperature regime where the system is magnetically ordered. In this regime the voltage response is hysteretic and history dependent. The behavior of the system suggests a percolative transport through regions of magnetically ordered droplets and/or strips separated by thin charge-ordered regions which melt under the action of a strong electric field.

Thin films of $Pr_{0.7}Ca_{0.3}MnO_3$ and $Pr_{0.7}Ca_{0.27}Sr_{0.03}MnO_3$ were deposited on (001) cut strontium titanate substrates using the technique of pulsed laser deposition. Standard $\theta - 2\theta$ x-ray diffraction and Rutherford backscattering (RBS) techniques were used to establish the crystallographic structure and chemical composition of the films, respectively. For the measurements of resistivity and current-voltage (I-V) characteristics, large area silver pads were evaporated on 2.5×8 mm^2 films through two shadow masks of width 50 and 150 μm. The silver-coated films were subsequently annealed at 400 °C in flowing oxygen. The measurements have been done in constant voltage as well as constant current modes. In the first case, a fixed or variable voltage was impressed on the sample and the current flow monitored by measuring the voltage drop across a metal film resistor. The constant current mode measurements of magnetoresistance were carried out in the temperature range of 4.2 to 300 K and with magnetic-field strength up to 4 Tesla.

The compound $Pr_{0.7}Ca_{0.3}MnO_3$ in its bulk ceramic and single-crystal forms undergoes a robust charge-ordering transition near 205 K.[16,17] This is followed by antiferromagnetic (AFM) ordering at ~140 K, and finally a ferromagnetic moment develops below ~120 K. While thin films of ferromagnetic hole-doped manganites have been studied extensively,[14,18] not much is known about the films of this compound. We have measured the temperature dependence of the electrical resistivity of a large number of $Pr_{0.7}Ca_{0.3}MnO_3$ films. The functional form of the resistivity below ~210 K is thermally activated with a barrier height of ~0.16 eV. For $T < 70$ K the sample resistance becomes so high that no current flows even at a field as high as 1×10^5 V/cm. In the inset of Fig. 1 we show the ρ vs T curve of a $Pr_{0.7}Ca_{0.3}MnO_3$ film. A small but distinct change in the slope of the curve at $T \sim 205$ K can be associated with the onset of the CO state. Unlike the case of single crystals where a distinct conducting state develops at $E > 1 \times 10^3$ V/cm,[11] the persistence of a highly resistive state in these films even at much higher fields in perhaps due to a substrate-induced strain, which may pin the CO state. Some thick films (~1 μm) of this compound when annealed at T

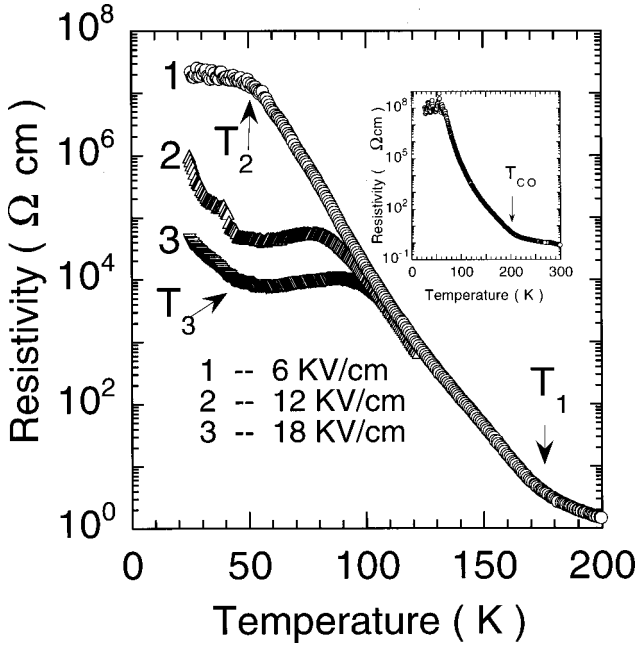

FIG. 1. Electrical resistivity of a $Pr_{0.7}Ca_{0.27}Sr_{0.03}MnO_3$ film measured as a function of increasing temperature at three values of the electric field. The inset shows the resistivity of a $Pr_{0.7}Ca_{0.3}MnO_3$ film.

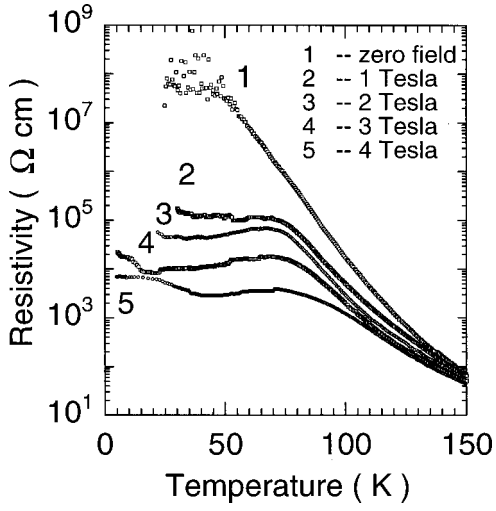

FIG. 2. Electrical resistivity of a $Pr_{0.7}Ca_{0.27}Sr_{0.03}MnO_3$ film in the presence of a magnetic field (curves 2–5) and in zero field (curve 1) conditions. The zero-field measurement was done in a constant voltage mode.

$>900\,^{\circ}C$, switched to a low resistivity state at high voltages. But the behavior was highly sample dependent.

The charge-ordering phenomenon is a consequence of the reduction in the overlap integral between d_{z^2} orbitals of the neighboring Mn^{3+} and Mn^{4+} ions through the bridging oxygen $p\sigma$ orbitals.[19] The loss of the kinetic energy of e_g electrons due to a decreased e_g band width is, however, recovered by the formation of two interpenetrating pseudocubic sublattices of Mn^{3+} and Mn^{4+} ions. The sublattice structure precludes a charge transfer as it would be self-destructive. The robustness of the charge-ordered state can be marginalized, however, by reducing the inward tilt of the Mn^{3+}—O—Mn^{4+} bonds through an increase in the d_{z^2}-$p\sigma$-d_{z^2} overlap. This has been achieved through substitution at the divalent or trivalent cation sites without changing the Mn^{3+}/Mn^{4+} ratio.[5,7,20,21] In the present study, we have substituted some of the Ca^{2+} sites in the compound $Pr_{0.7}Ca_{0.3}MnO_3$ with Sr^{2+}, which has a much larger ionic radius. The fully substituted compound $Pr_{0.7}Sr_{0.3}MnO_3$ is a ferromagnetic metal.[17] Figure 1 shows the resistivity of a ~5000-Å-thick film of the compound $Pr_{0.7}Ca_{0.27}Sr_{0.03}MnO_3$ measured as a function of increasing temperature in the constant voltage mode. Two distinct regimes of behavior can be identified in the data taken at the lowest field. Between 25 K and T_2, the resistivity shows a slow drop with temperature followed by a marked thermally activated conduction between T_2 and T_1. A distinct change in the slope of the curve at T_1 suggests transition from the charge-ordered to charge-localized paramagnetic state as seen in the case $Pr_{0.7}Ca_{0.3}MnO_3$ film. When the electric field is increased by a factor of 2, a considerably lower value of ρ is seen at 25 K. The resistivity drops with increasing temperature till a minimum is reached at T_3, and then a metal-like behavior follows over a small range of temperatures. Measurements at the next higher field show that the metal-like regime is wider and the resistance at T_3 is considerably lower. At temperatures above 100 K, the behavior of ρ at all fields is similar.

In Fig. 2 we show the resistivity of an identical sample measured in the presence of a magnetic field applied parallel to the direction of current. These are constant current measurements in which the electric field was kept below ~200 V/cm. Further, the maximum resistance measured in these experiments is 1% of the input impedence (10 G Ω) of the voltmeter used. In order to highlight the drastic effects of a magnetic field on the resistivity, Fig. 2 also shows the zero-field data for the same sample. This measurement, however, had to be done in the constant voltage mode (E ~4 KV/cm) because of the impedence-related limitations of the constant current method. In zero magnetic field, the resistivity of the sample is thermally activated over the entire range of temperature. At the 1 Tesla field it shows a plateau below ~50 K. On increasing the field further, a metal-like behavior is observed over a limited temperature range between ~35 to ~75 K. There is a striking similarity in the data shown in Figs. 1 and 2. The effects of electric and magnetic fields on charge transport are complimentary.

In the regime of temperatures below the shoulder in ρ which is marked by T_2 the resistivity shows a highly nonlinear behavior. In Fig. 3 we show a series of I-V curves taken at several temperatures. For each of these measurements, the sample was first cooled in zero electric field to the desired temperature, and then the field was scanned at a constant rate from zero to a maximum value followed by a reverse scan to zero field. As evident in the figure, the sample shows a remarkable switching to a low resistance state when a critical value of the electric field is reached. This is highlighted by the logarithmic scale used for the y axis. On field reversal, however, the behavior is hysteretic with the current following the Ohm's law. This point has been emphasized by plotting the 25-K data on a linear scale as well. Subsequent field scans at the same temperature and also at higher temperatures do not reveal the hysteresis. The behavior remains Ohmic in both directions of the field scan. The high resistiv-

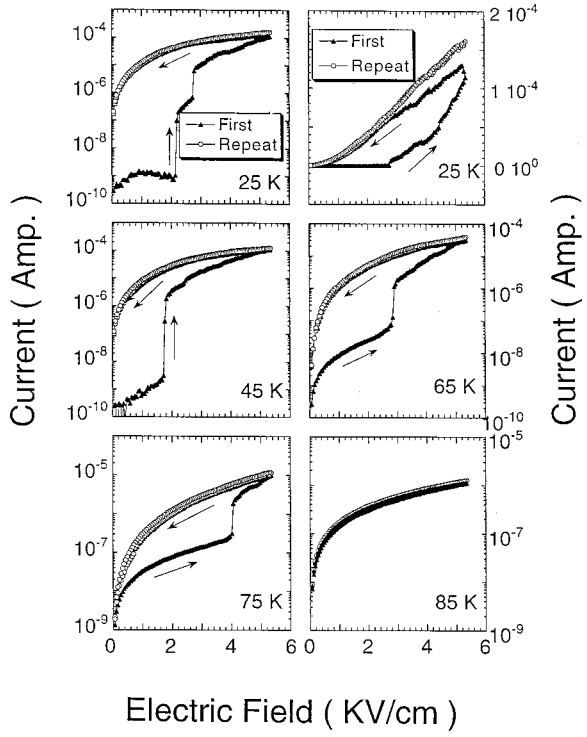

FIG. 3. Current-voltage characteristics of a $Pr_{0.7}Ca_{0.27}Sr_{0.03}MnO_3$ film at several temperatures. The data taken at 25 K are shown in linear as well as logarithmic scales (top two panels).

ity state, the off state, is, however, recovered if the sample is warmed up to temperatures above T_1. The I-V curves show three characteristic features on increasing the temperature: (i) the switching field to the low resistivity state decreases, (ii) the area under the hysteresis shrinks, and (iii) at temperatures above ~85 K the behavior is fully reversible. An additional feature of the data shown in Fig. 3 is the steplike increase in current at certain values of the electric field. In semiconductor physics, such steps are associated with the emptying of the midgap traps by the electric field. In the present case, however, the value of the electric field at which the steps occur is sample and history dependent. In the present scenario, the steps presumably correspond to the opening up of percolative paths in the sample in which the conductivity is metal-like. The dynamics of the system is such that the channels remain open in the reverse branch of the field scan.

An interesting aspect of the metastability and consequent history effects is revealed if the resistance of the samples is measured in a cyclic manner. Figure 4 shows the behavior of resistivity at a fixed electric field over four regimes covering the temperature ranges 25–50 K, 25–100 K, 25–200 K, and 25–100 K. The procedure involved measurement of $\rho(T)$ up to the highest temperature of the first range, followed by cooling to 25 K in the zero electric field and then measurement up to the highest temperature of the next range. In the first regime, while a large irreversibility is seen in the resistivity, the behavior is nearly reversible in the subsequent two regimes. In the last regime, however, the pristine state of the sample is recovered on cooling. The critical temperature above which a full recovery takes place is higher than the charge-ordering temperature (~175 K) of the system.

The observed similarity between the effects of the electric

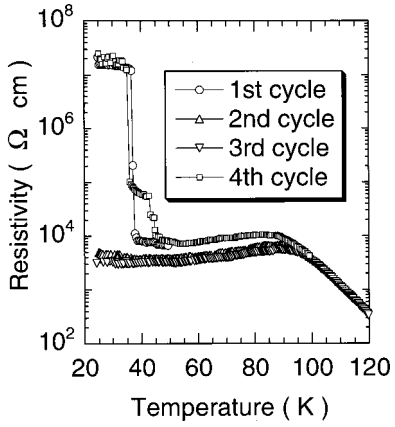

FIG. 4. History effects in the resistivity of a $Pr_{0.7}Ca_{0.27}Sr_{0.03}MnO_3$ film. The resistivity was measured at a constant electric field (2 KV/cm) in four successive cycles covering the temperature ranges 25–50 K, 25–100 K, 25–200 K, and 25–100 K.

and magnetic fields on the current transport in this system is a result of a delicate interplay between the spin and charge-ordering effects. The charge-ordered state is the most robust at half filling ($x=\frac{1}{2}$) in the manganite system $Pr_{1-x}Ca_xMnO_3$.[8,22] At $x=0.3$, however, the number of Mn^{3+} ions exceeds the number of Mn^{4+} ions and a topological hindrance in the formation of a CO state ensues. The incorporation of Sr further weakens the formation of the charge-ordered state because of its larger ionic radius. Based on the reported structural and magnetic measurements on $Pr_{0.7}Ca_{0.3}MnO_3$,[16] it can be argued that the evolution of the system on cooling follows the following sequence of events. On cooling below T_{CO} the system goes to a disordered CO state comprised of inclusions where Mn^{4+} and Mn^{3+} ions are distributed randomly. At lower temperatures ($\sim T_2$) an AFM ordering develops and at a still lower T, a ferromagnetic component evolves primarily from the ordering of spins in the inclusions. Such regions where the conductivity is controlled by the double-exchange mechanism have been variedly called as clusters or droplets or strips. The presence of such magnetic inhomogenity in doped manganites has been established through neutron scattering,[10,16,17,23–26] electron diffraction,[8,27] nuclear magnetic resonance,[24] and scanning probe microscopies.[27,28] Preliminary measurements of magnetization of our films reveal magnetic ordering below ~100 K.[29] These transport data suggest that at the lowest temperature of measurement, the ferromagnetic strips do not form a percolative channel through the sample. The behavior is more like that of a system consisting of ferromagnetic clusters in a dielectric matrix.[30] Strong electric field seems to melt the thinnest CO regions separating the droplets and/or strips, causing a surge of current through the sample. Clear evidence of this is seen in the I-V curves. The observation of an increase in magnetization when the sample switches to the conducting state supports this argument. The conducting channels remain open even after the electric field is removed. This is why the reverse branch of the I-V curves is Ohmic. Evidence for the occurence of such permanent changes even after the driving force is removed is also seen in experiments where the CO to CD transition is induced by irradiation with electrons,[8] x ray,[10,16] and visible photons.[9] The observed hysteresis is a manifestation of the melting of the CO regions.

Once a conducting channel is opened up, the resistivity shows a metal-like behavior up to a temperature where the internal Weiss field is strong enough to maintain ferromagnetic ordering in the clusters and also suppress CO in the thin regions of film separating the clusters. The role of electric and magnetic fields is alike in this regard. At higher temperatures, the CO state gains strength at the expense of a weakening Weiss field and charge ordering is reestablished in the thin regions. This blocks the metal-like percolative channels. The thermally activated resistivity beyond temperature T_2 clearly supports this viewpoint.

In summary, we have observed electric-field-induced switching from a high to a low resistivity state in thin films of the manganite $Pr_{0.7}Ca_{0.27}Sr_{0.03}MnO_3$. This sharp decrease in the resistivity triggered by the electric and magnetic fields is restricted to a regime of temperature where the Mn^{3+} and Mn^{4+} spins are ordered. The observation of hysteresis in the I-V curves and the history effects seen in the measurements of $\rho(T)$ suggest an inhomogeneous medium where charge-ordered and ferromagnetically ordered regions grow at the expense of each other and lead to a percolative transport.

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