

Current-induced phase control in charged-ordered $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ crystals

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Single crystals of $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ show current-induced insulator–metal (IM) transitions at low temperatures. In addition, the charge-ordering transition temperature, T_{co} , decreases with increasing current. The electroresistive ratio, defined as $\rho_{0.5}/\rho_I$ where $\rho_{0.5}$ is the resistivity at a current of 0.5 mA and ρ_I the resistivity at a given applied current, I , varies markedly with temperature and the value of I . Thermal hysteresis observed in $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ at the IM transition indicates that the transition is first order. The current-induced changes are comparable to those induced by magnetic fields, and accordingly the IM transition in $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ is associated with a larger drop in resistivity. © 2004 American Institute of Physics. [DOI: 10.1063/1.1641515]

Phase control in manganates of the type $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln=rare earth, A=alkaline earth) can be achieved by suitably choosing the Ln and A cations which control the bandwidth as well as the bandfilling. Thus, appropriate A-site cations can lead to wide bandwidth conductors exhibiting ferromagnetism (FM) and metallicity through the double exchange mechanism. Charge ordering can be induced by reducing the bandwidth owing to its origin to Coulomb repulsion, orbital ordering, and Jahn–Teller distortion. The charge-ordered (CO) state is generally associated with antiferromagnetism (AFM) and insulating behavior.¹ The control of phases in the manganates, which can lead to tunable electronic properties, is achieved by subjecting them to external stimuli such as magnetic fields,² irradiation by high-power lasers,³ and chemical substitution.^{4,5} The stimuli transform the CO state to a ferromagnetic metallic (FMM) state. The effects induced by electric fields have been studied in the CO as well as the FMM states of the manganates.^{6–9} The electric current drives these materials to a low resistive state, the conductive nature arising from the tunnel junctions separating neighboring ferromagnetic domains or due to the percolative nature of the conductive state.

Since the effects of electrical fields on the CO rare-earth manganates are somewhat unique, we considered it important to investigate the effects of passing electrical currents through single-crystals of CO materials in detail. In particular, we were interested to find out whether electric fields affect the CO transition, and whether the nature of the insulator–metal (IM) transition depends on the average radius of the A-site cations, $\langle r_A \rangle$. For this purpose, we have chosen $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, wherein the former with a $\langle r_A \rangle$ of 1.172 Å shows a robust CO state with a charge-ordering transition temperature, T_{co} , of 240 K which cannot be melted even under high magnetic fields of 25 T or greater. On the other hand, $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ ($\langle r_A \rangle$

= 1.18 Å) has a T_{co} of 230 K, with the CO state transforming to a FMM state at fields of 6–12 T. A comparison of the electric field effects on these two manganates is of interest, especially since an electric field-induced IM transition is accompanied by the appearance of magnetization.¹⁰

Single crystals of $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ were grown with a floating-zone melting furnace. The crystals thus obtained were cut and annealed in oxygen for 48 h. Electrical resistivity measurements were carried out on crystals 4 mm in diameter and 1 mm in thickness, by the four-probe method. The resistivity was measured in two ways. The sample was cooled under a constant current, I , and upon reaching the lowest temperature, and the data were collected (1) in the warming cycle without switching off the current, or (2) after switching off the current before starting the warm-up cycle at the same current.

In Fig. 1(a), we show the resistivity of a $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ crystal at different applied currents when the sample is cooled from 300 to 15 K. There are four distinct features in the plot. There is a drop in the resistivity throughout the temperature range as the current, I , is increased. The temperature dependence of the resistivity changes with the increase in I . An IM transition occurs around 65 K (T_{IM}) at values of I , beyond a threshold value. The T_{co} decreases with increasing I .

The decrease in the resistivity with an increase in I is not due to Joule heating as seen from the low-temperature metallic regime close to T_{IM} in Fig. 1(a). The resistivity at a given I increases with increasing temperature, while at a given temperature, it decreases with increasing I . The opposite would be true for Joule heating. Also, the T_{IM} does not vary with increasing I although resistivity decreases drastically.

The negative differential resistance, i.e., the decrease in resistivity with increasing I observed beyond a certain value of I , is due to the presence of metallic filaments, which are ferromagnetic and carry most of the current.⁸ The high value

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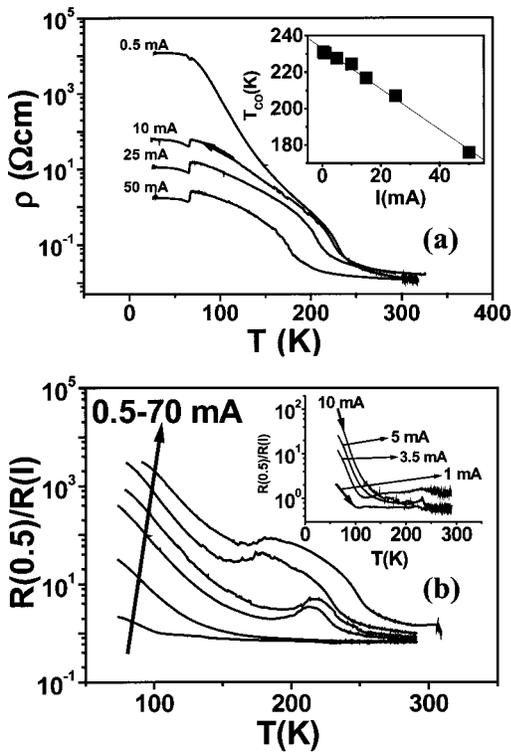


FIG. 1. (a) Temperature variation of the resistivity of $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ in the cooling runs. The inset shows the variation of T_{co} with the applied current. (b) Variation of the electroresistive ratio with temperature in the cooling cycle. The inset shows the same in the heating cycle.

of the resistivity below T_{IM} is attributed to the coexistence of the ferromagnetic and CO insulator phases.¹¹ The relative fraction of the FMM phase increases with increasing current causing a lowering of resistivity below the T_{IM} .¹² The small rise in resistivity below the IM transition may be attributed to the tunneling of electrons between the FMM clusters through CO insulating clusters, wherein an interplay between spin-dependent tunneling and charge localization controls the resistivity of the sample. This is corroborated by the temperature variation of the resistivity below 50 K which shows an $\exp(1/\sqrt{T})$ dependence.¹³

The T_{co} shifts to lower values with increase in I , becoming constant beyond a high I value (~ 50 mA). Such a current-induced shift in T_{co} is noteworthy. The plot of T_{co} against I [see the inset of Fig. 1(a)] is linear with a slope of ~ 1 K/mA. The decrease in the T_{co} could be due to the charge delocalization driven by an external current which in turn decreases the lattice distortion. The lowering of lattice distortion due to the substitution at the A site in $(\text{La}_{1-x}\text{Pr}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ gives rise to a FM transition at low temperatures.¹⁴ We observe a similar behavior in the CO manganates where the increasing current lowers the lattice distortion and favors the FMM state [Fig. 1(a)].

As the current through the $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ crystal is increased, a drastic change in the resistivity is observed. The electroresistive ratio, $\rho_{0.5}/\rho_I$, where $\rho_{0.5}$ is the resistivity at a current of 0.5 mA (which is the smallest I employed by us) and ρ_I the resistivity at a given applied current, I , varies with temperature as shown in Fig. 1(b). The change in resistivity

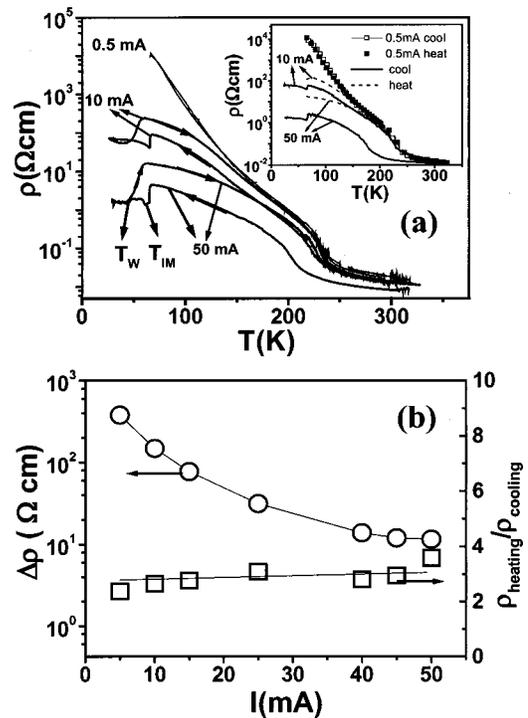


FIG. 2. (a) Temperature variation of resistivity of $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ in the cooling and heating cycles, wherein the current is not switched off at the lowest temperature before starting the heating run. The inset shows the same with the current switched off and then switched on at the lowest temperature, before starting the heating run. (b) The squares represent the ratio of resistivities at the peak value in the cooling and heating runs with the current not switched off before starting measurements at the lowest temperature. Open circles represent the difference in the peak values of resistivity, $\Delta\rho$.

at 20 K is four orders of magnitude while it is one or two orders at $T \approx T_{\text{co}}$. The four orders of magnitude change in the resistivity is achieved by changing the applied I by two orders, indicating the nonohmic behavior. As the I is increased, there is a sharp drop in resistivity of the sample at T_{IM} [Fig. 2(a)], a behavior not observed earlier.

When the ρ - T data are recorded in the warming run without turning off the current, we observe a thermal hysteresis, which becomes prominent at a large I . The observation of hysteresis suggests a first-order nature of the transition induced by electric currents. In the warming run, the low resistive state persists down to a temperature T_W , lower than T_{IM} [Fig. 2(a)]. The hysteresis observed here is somewhat different from that in a normal ferromagnetic metal at the IM transition. The higher transition temperature in the cooling cycle relative to the warming cycle is attributed to the competing FM and AFM correlations.¹⁵ The current-induced hysteresis in the present case is also due to such a competition near T_{IM} . The resistivity change at T_W increases with the increasing I , but T_{IM} and T_W are both independent of I , as also the ratio of the peak resistivity in the heating and the cooling runs. If one compares the change in the resistivity to the ratio of resistivities, the phenomenon becomes striking [Fig. 2(b)].

When the current is switched off at a low temperature, the resistivity of the sample becomes high and the current source is not able to pass the same current due to voltage

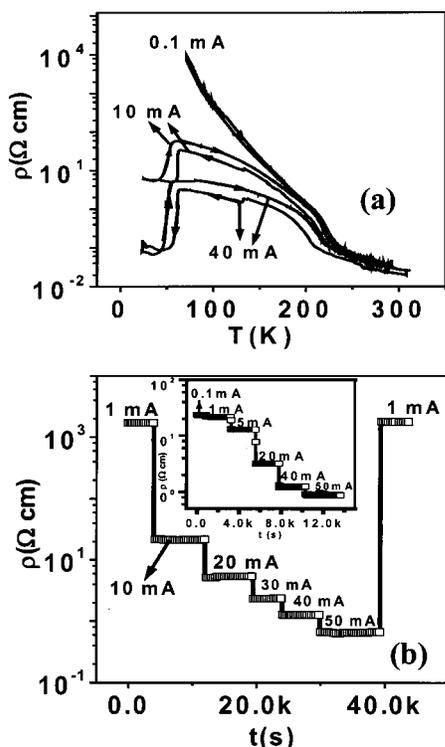


FIG. 3. (a) Temperature variation of resistivity of $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ at different currents. (b) Variation of the resistivity at 20 K with time at different currents. The inset shows the same at 150 K.

limit (V -limit 105 V) of the source. The effect of I in the warming run is quite different from that in the cooling run, the resistivities in the former being higher. Although the resistivity of the sample shows field-dependence, the ρ - T curves merge around 150 K, above which the current has little effect [inset in Fig. 2(a)]. This is in contrast to the cooling data.

Current-induced effects on a $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ crystal are shown in Fig. 3(a). The effects are similar to those in $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ but the drop in resistivity at low temperatures is considerably more marked. The IM transition observed in the CO crystals is not due to Joule heating or other thermal effects, as the crystals kept at 20 K at different currents for 1–2 h showed no change in resistivity, although the resistivity decreased with increasing I [Fig. 3(b)]. When I was decreased to the initial value, the resistivity attained the value at $t=0$, thereby showing that the switching was associated with a memory. The time dependence resistivity at 150 K shows a behavior similar to that at 20 K [inset of Fig. 3(b)].

The results of the present study are as follows. Passing relatively high I through the CO manganates, causes an IM

transition, independent of the $\langle r_A \rangle$, unlike the effect of magnetic fields.¹ The electroresistive ratio increases with increasing I where as the T_{co} decreases with increasing I . The magnitude of drop in the resistivity at the IM transition parallels the effect of magnetic fields in some respect. $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ contains two phases below T_{co} ,¹⁶ and FM correlations are present at low temperatures.^{1,17} The presence of two phases below T_{co} , in $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ with one phase having spin-glass like features has been reported.¹⁸ On the application of a reasonably high I , metallic domains grow in size. Such a metal-like phase generated by electric fields will also be magnetic.¹⁰ The metal-like conduction around 65 K may be facilitated by the separation of FMM, CO insulator, and paramagnetic phases.¹¹

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