

Nonlinear conduction in charge-ordered $\text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3$: Effect of magnetic fields

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Nonlinear conduction in a single crystal of charge-ordered $\text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3$ has been investigated in an applied magnetic field. In zero field, the nonlinear conduction, which starts at $T < T_{CO}$, can give rise to a region of negative differential resistance (NDR) which shows up below the Néel temperature. Application of a magnetic field inhibits the appearance of NDR and makes the nonlinear conduction strongly hysteretic on cycling of the bias current. This is most severe in the temperature range where the charge-ordered state melts in an applied magnetic field. Our experiment strongly suggests that application of a magnetic field in the charge-ordering regime causes a coexistence of two phases.

Rare-earth manganites with general chemical formula $R_{1-x}A_x\text{MnO}_3$ have attracted current interest because of rich variety of phenomena like colossal magnetoresistance (CMR) and charge ordering (CO).^{1,2} For certain values of x , close to 0.5, these compounds undergo a first-order charge-ordering (CO) transition where the Mn^{3+} and Mn^{4+} species arrange themselves alternately in the lattice. This transition leading to charge localization occurs on cooling below a temperature T_{CO} , referred to as the charge-ordering temperature. Orbital ordering also accompanies the charge ordering and a long-range antiferromagnetic (AFM) order sets in at lower temperature ($T_N < T_{CO}$). (For some systems, like $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, $T_N = T_{CO}$.¹) The system studied by us, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.37$), happens to be a unique charge-ordered system in which the charge-ordered state remains insulating for all values of x due to its low tolerance factor. It shows both charge and orbital order below $T_{CO} = 240$ K and the AFM order occurs at $T_N = 175$ K.

A fascinating aspect of the charge-ordered/orbital ordered state is that the charge-ordered insulator (COI) phase is unstable to a number of external perturbations (like magnetic field,¹ electric field,^{3,4} optical radiation,^{5,6} etc.) and can be melted by them. An application of the magnetic field leads to a collapse of the charge-ordering gap (Δ_{CO}) and there is an insulator-metal transition (melting) of the COI state to a ferromagnetic (FM) state.^{7,8} Optical radiation seems to create conducting filaments which at low temperatures leads to nonlinear transport and even at much lower temperatures a region of negative differential resistance (with $V \sim I^{-n}$ with $0 < n < 1$).^{5,6} Application of an electric field also gives rise to nonlinear conduction, which seems to have a threshold field associated with it and a broad band noise of substantial magnitude with a power spectrum $\sim 1/\text{frequency}$.⁹

A schematic of the phase diagram of the material in the H - T plane studied is shown in the inset of Fig. 1. In a given field H , the COI state melts into the FM phase at the melting temperature T_{MH} (marked in the figure). We designate the region $T_{MH} < T < T_{CO}$ with $H \neq 0$ (shaded in inset) as the ‘‘mixed charge-ordered’’ (MCO) region to distinguish it

from the COI ($H = 0, T < T_{CO}$) state as well as from the FM state ($H \neq 0, T < T_{MH}$). We call it the MCO region because we will show below that the region has co-existence of two phases. In this paper we address the specific question of the nature of nonlinear electronic transport in the COI as well as MCO region for $T < T_{MH}$. We have performed experiments along a constant H line. In particular, we observe that in the COI state, transport is strongly nonlinear with a negative differential resistance (NDR) developing for $T < T_N$ while in the MCO state, the NDR is strongly inhibited. In addition, in the MCO state there is a large hysteresis in the I - V characteristics seen on cycling of the bias current. We ascribe this to creation of a co-existing two phase region in the mixed state. (Hysteresis seen in the I - V curve on cycling the bias current is distinct from the hysteresis in resistivity seen on H field cycling in most past experiments.)

Our sample was a ($4 \times 2 \times 0.3$ mm³) single crystal of $\text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3$ grown by the floating-zone technique. Four linear contact pads of Ag-In alloy was soldered on to the sample in linear four-probe configuration with separation ≈ 0.25 mm. I - V data were taken with current biasing and with a temperature control better than 10 mK. To avoid any memory effects, the sample was heated well above T_{CO} , before recording the I - V data at each temperature and magnetic field. We have also measured electrical noise by digitizing the voltage across the sample voltage probes. The power spectrum was obtained by Fourier transform of the time autocorrelation function of the voltage after subtracting out the mean. The magnetic-field measurements were done using cryogen-free superconducting magnet capable of producing field up to 15 T. In this paper, to limit the scope of data being presented, we report data only for a field of 8 T, which in the temperature range of investigation encompasses all the phases that we need to study.

Figure 1 shows the resistivity (ρ) as a function of temperature for various magnetic fields. For $H = 0$, $T_{CO} \approx 240$ K. In a field of 8 T, the $T_{CO} \approx 210$ K and the CO state completely melts to the FM state at 80 K. We identify this temperature as T_{MH} for the 8-T field. A magnetic field of 12

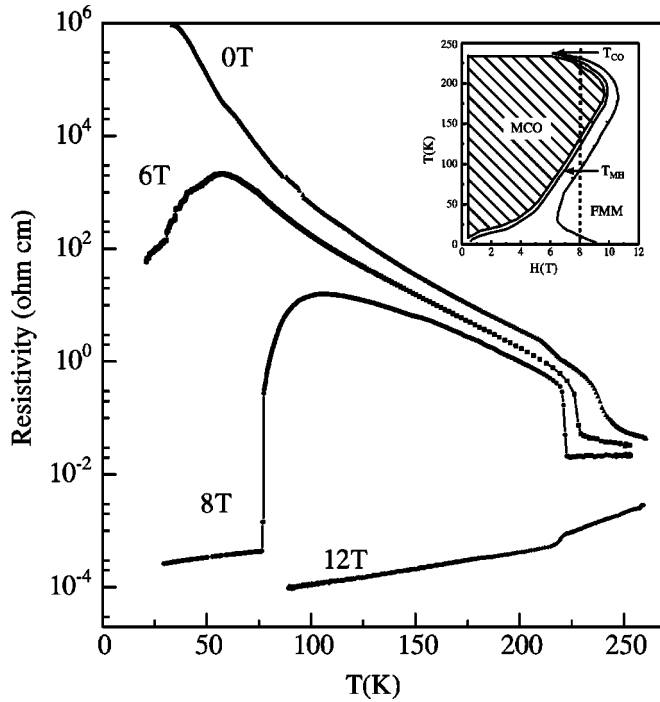


FIG. 1. Resistivity as a function of T in different magnetic fields for the sample $\text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3$. The inset shows the schematic phase diagram.

T arrests the formation of CO state and the sample remains metallic at all temperatures. The observed data are in agreement with previous studies done on the $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system.⁷ (Note that magnetic susceptibility shows a transition near $T \approx 240$ K, $T_N \approx 175$ K.)

Figure 2 shows the I - V characteristics at different temperatures in zero magnetic field. The I - V characteristics are

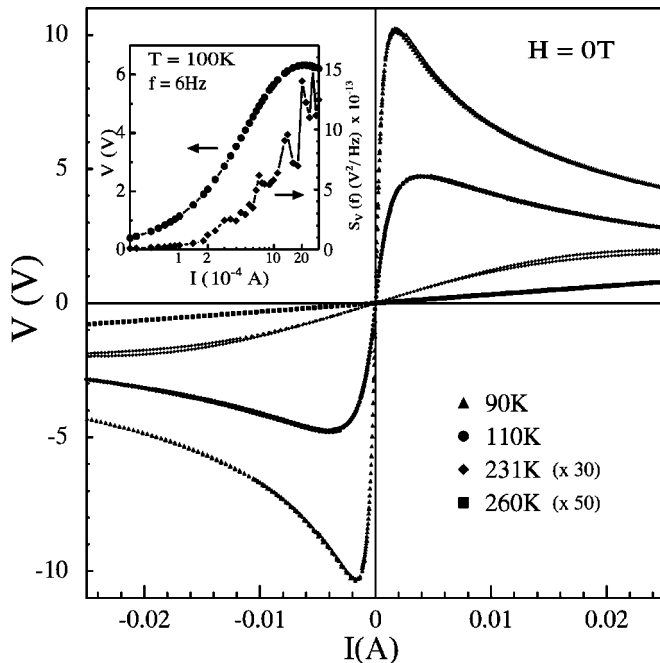


FIG. 2. The I - V curves showing nonlinear conduction and negative differential resistance. The inset shows the appearance of large noise at the onset of nonlinear conduction.

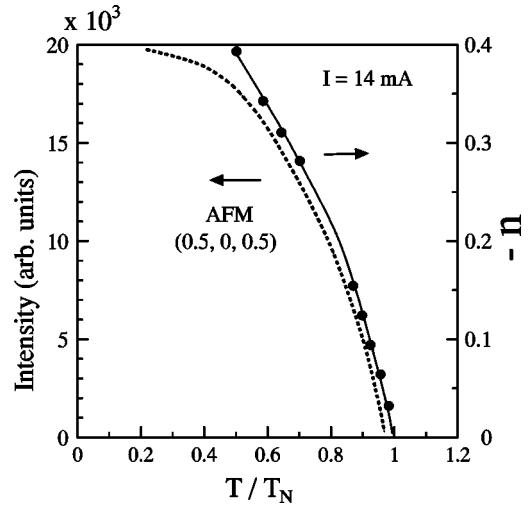


FIG. 3. Temperature dependence of the exponent n . The line shows the temperature dependence of the intensity of the $(1/2, 0/1/2)$ line obtained from the neutron experiment (Ref. 10).

linear for $T > 260$ K ($> T_{CO}$) and at all $T < T_{CO}$ (i.e., in the COI state), nonlinear conduction is observed. One can identify a threshold electric field or a current density beyond which the conduction is strongly nonlinear as reported earlier in films of $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.⁹ In the inset of Fig. 2, we show the noise power measured at 6 Hz as a function of biasing current I . At the onset of the nonlinear conduction the noise increases rather rapidly. The noise has a $1/f$ character for $0.02 \text{ Hz} < f < 20 \text{ Hz}$. Appearance of a strong noise component is a characteristic of the melting process.

At $T < 170$ K, a new component gets added to the nonlinearity and a region of negative differential resistance ($dV/dI < 0$) is observed when the bias current I exceeds a current threshold (I_{TH}). I_{TH} decreases as T decreases and at $T = 85$ K, $I_{TH} \approx 1.2$ mA corresponding to a current density $\approx 0.5 \text{ A/cm}^2$. In the region of negative differential resistance (NDR), for $I > I_{TH}$, $V \propto I^{-n}$, where $0 < n < 1$. The I - V characteristics are symmetric and exhibit no hysteresis on current cycling except for T close to T_{CO} . The observed data are highly reproducible. Interestingly, there are several similarities of NDR state created by current and that created by optical radiation using a laser.⁵ We find that the exponent n , which is a measure of the NDR ($d \ln V / d \ln I = -n$), has a strong temperature dependence. In Fig. 3 we show n as a function of temperature T scaled by T_N . We find that $n \rightarrow 0$ as $T/T_N \rightarrow 1$ and for $T/T_N \gg 1$, $n \rightarrow \text{constant} (\approx 0.5)$. A likely explanation for occurrence of NDR can be that for $I > I_{TH}$ metallic filaments open up. These filaments being of lower resistance will provide parallel paths of conduction. This extra current path will decrease the voltage drop across the sample for a given current. As the current increases presumably more such channels open up leading up to a further decrease in V . This will manifest itself in the I - V curve with a region of NDR. Nonlinear conduction can also occur due to depinning of CO domains above a threshold applied field as has been reported earlier.⁹ But in the region of NDR, we assume conduction through metallic filaments to be the dominant mechanism for nonlinear conduction. The formation of the conducting filament is not a breakdown as the I - V curve is reproducible on cycling. A similar mechanism is

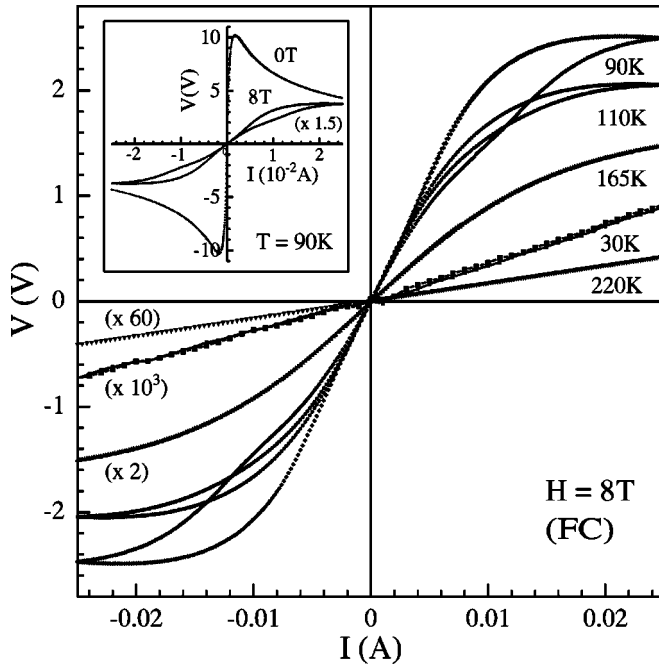


FIG. 4. The nonlinear transport in a magnetic field of 8 T. The inset shows a comparison of the I - V data at $T=90$ K in zero field and in $H=8$ T.

proposed for optically produced NDR.⁶ In an optically melted CO state in the NDR regime, $I \propto V^{-n}$ with $n \approx 2/3$ at $T=10$ K.⁶ Given the similarity, it is expected that both have the same origin.

We have measured the temperature rise of the sample with respect to the base (ΔT) by attaching directly a thermometer to the sample. $\Delta T \leq 20$ K at the lowest temperature (≈ 80 K) and at the highest power dissipation level (0.1 W). At 150 K, $\Delta < 10$ K and it is negligible for $T \geq 180$ K. The power dissipation level where the NDR sets in at the lowest temperature leads to a $\Delta T \approx 5$ K. We also investigated whether the NDR is caused by this heating effect and rule out heating as the cause for the NDR. However, the heating can have some influence on the value of n at the highest measuring current.

It appears that a strong correlation exists between the onset of the NDR regime and the magnetic order at T_N . We illustrate this in Fig. 3 where we plot the temperature dependence of the intensity of the (0.5.0.5.0) line as obtained from the neutron diffraction¹⁰ in a sample of $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$. The temperature dependence of the intensity of this line is a measure of the growth of the AFM order below T_N . It is clearly seen from the figure that not only does $n \rightarrow 0$ at $T = T_N$, it also follows a temperature dependence which closely matches that of the growth of the AFM order as observed through neutron diffraction. There may be two likely reasons for the appearance of NDR below T_N . One reason can be that for $T < T_N$ there may be incommensurate to commensurate transition of the CO or orbital order as has been reported in a closely related composition $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.¹¹ The incommensuration which is due to disorder in orbital ordering can inhibit formation of such conducting filaments as are needed for the NDR. Alternatively, the AFM order in these materials being of pseudo-charge exchange (CE) type,¹² there is a FM coupling be-

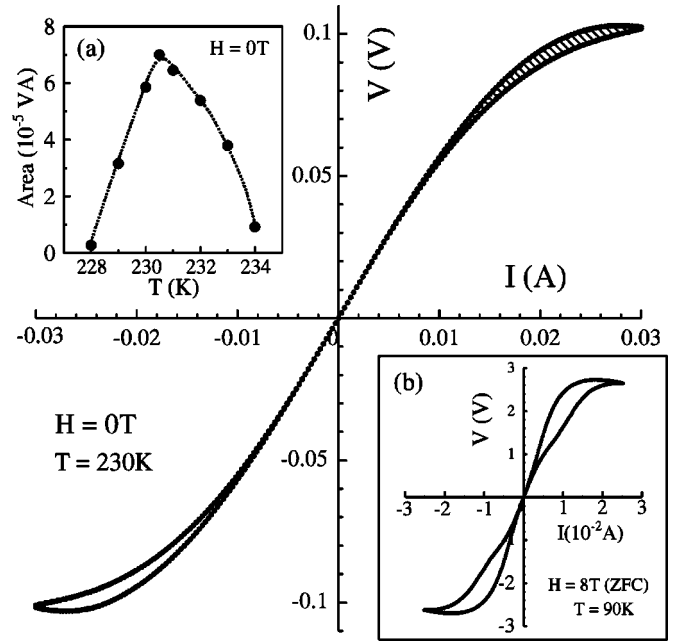


FIG. 5. Hysteresis observed in the I - V curves on cycling of the bias current. The inset (a) shows the temperature dependence of the area under hysteresis close to T_{CO} . The inset (b) shows the hysteresis in I - V curve in a magnetic field.

tween the planes which contain zigzag AFM chains. It may be that below T_N this interplane FM coupling enhances the formation of the metallic filaments which can be made up of FM phases. If the later hypothesis is true we will not see formation of NDR region in CO systems with CE-type AFM order which has only AFM coupling between planes.

Figure 4 shows the I - V characteristics at different temperatures in an 8-T magnetic field. In the MCO state, the nonlinear conduction persists and is qualitatively similar to that found in COI. For both $T > T_{CO}$ and $T < T_{MH}$ the I - V behavior is linear, but the two states have ρ differing by two orders of magnitude. [All the data were taken after field cooling (FC) in $H=8$ T from $T=300$ K. At each temperature, the sample was freshly prepared as a FC sample after warming it up to room temperature to avoid any memory effect.] There is a distinct memory of the previously applied field when the field is changed in the COI state and on warming up beyond T_{CO} one can erase the memory. Experiments were also carried out under zero-field-cooled (ZFC) conditions. The I - V characteristics for both FC and ZFC are qualitatively similar, and the ZFC curve consistently shows higher V (for a given I) than the corresponding FC curve at each T . Given the limited scope of this paper we do not discuss the details here.

The inset of Fig. 4 shows a comparison of the I - V curves of the COI and the MCO states at a representative temperature. The COI and the MCO state differ significantly in two aspects, there is no NDR at any temperature in the MCO state at 8 T and there is strong hysteresis in the I - V curve in the MCO region.

An important observation of this investigation is that the melting of the CO state either by temperature ($T \approx T_{CO}$) or by a magnetic field is accompanied by strong hysteresis behavior in the I - V curve (i.e., the I - V curves do not follow each other during current ramping up and down the cycle.

This is different from the hysteresis seen on H cycling). This can be seen in Figs. 4 and 5. The hysteresis does not depend on the speed with which the current is ramped up and down. Typically in our experiment one cycle is taken over 40 min. The area under the hysteresis curve is defined as the hatched region in Fig. 5. We plot the area under the hysteresis curve as a function of T in the inset of Fig. 5. It is clearly seen that in the COI state, the hysteresis is observed only for $\Delta T \approx 10$ K below T_{CO} . In contrast, in the MCO state, hysteresis persists over an extensive temperature range above T_{MH} . In the inset of Fig. 5 (b), we show an example of the hysteresis in the MCO state as $T \rightarrow T_{MH}$ from above.

The appearance of hysteresis in the I - V curves can be interpreted as due to the co-existence of two phases in the MCO region. There is evidence of such co-existing phases in the TEM data taken near T_{CO} in (La,Ca)MnO₃ and (Pr,Ca)MnO₃ systems near the melting transition ($T \approx T_{CO}$).¹³ In this material under study, it has been seen that the ferromagnetic spin correlations persist below T_{CO} .¹⁰

This is stabilized by the applied field and thus can be the nucleus of the FM phase. In the MCO state these nuclei get stabilized on cooling and then grow as the second phase. Eventually as $T \rightarrow T_{MH}$, the MCO state collapses to the FM phase. Existence of such co-existing phases will prevent the formation of the metallic filaments needed for the occurrence of NDR. As a result the NDR will be strongly suppressed in this region.

To summarize, we have carried out a systematic investigation of nonlinear transport in a CO system in a magnetic field. We find that a negative differential resistance region shows up below T_N which is inhibited by application of a magnetic field. In the region $T_{CO} < T < T_{MH}$, application of a magnetic field creates a region of co-existing phases leading to a strong hysteretic I - V curve which become substantial in the temperature regions close to T_{CO} and T_{MH} .

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